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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Selective Hydrogenation of Unsaturated Esters to Unsaturated Alcohols

BY JOHN SAUER AND HOMER ADKINS

The hydrogenation of the double bond in such a compound as ethyl oleate is readily accomplished at room temperatures and atmospheric pressures of hydrogen over nickel, platinum or palladium catalysts. In order to bring about satisfactorily the hydrogenation of a carbalkoxy to a carbinol group temperatures in excess of 200° and pressures of the order of 100 atmospheres are required. In other words the alkene linkage reacts with hydrogen under conditions which are as mild as are used in any catalytic hydrogenation, while the carbalkoxy group requires drastic conditions. However, it seemed worth while to attempt the selective hydrogenation of the carbalkoxy groups with certain of the metallic oxides which are relatively inactive in the catalysis of the hydrogenation of alkene linkages.[1]

There are recorded in Table I the results obtained with six such catalysts containing zinc or copper combined with chromium, vanadium or molybdenum. Ethyl or butyl oleates were used in testing the catalysts. The butyl ester is very much to be preferred for this purpose since the ethyl esters boil at so nearly the same temperature as the alcohols that it is difficult to separate the ester from the alcohols.

It may be seen from the data in the table that copper–molybdenum oxide induced the hydrogenation of the double bond with the formation of ethyl stearate, while copper–chromium oxide caused the addition of three moles of hydrogen with the formation of octadecanol. Zinc–chromium oxide was, however, relatively inactive toward the alkene linkage and reasonably active toward the carbalkoxy group so that the unsaturated alcohol $C_{17}H_{33}CH_2OH$ was obtained in yields of over 60%. An unsaturated alcohol $C_{21}H_{41}CH_2OH$ was obtained in similar yield from butyl erucate. Zinc–vanadium oxide and zinc–molybdenum oxide were similar but inferior to zinc–chromium oxide for the production of the unsaturated alcohol.

Thus it is seen to be feasible to prepare unsaturated alcohols by the hydrogenation of certain unsaturated esters. However, the process is not very satisfactory from a preparational standpoint. A very high ratio of catalyst to ester must be used. It is probable that one part of catalyst should be used for two parts of ester. The temperature required for adequate reaction is quite high (300°) and even so seven to eleven hours were required for relatively complete reactions. These factors have made it impossible to obtain yields higher than 68% of the unsaturated alcohol and in the case of the ester of undecen-10-oic acid, the yield was only 37%. The unsaturated alcohol produced by this process is always accompanied by small amounts of saturated alcohol which it appears cannot be readily separated from the unsaturated alcohol by fractionation. The process apparently is not applicable to esters

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(1) Lazier and Vaughen, THIS JOURNAL, **53**, 3719 (1931); **54**, 3080 (1932).

TABLE I

HYDROGENATION OF UNSATURATED ESTERS

Ester	G.	G.	Catalyst	Temp., °C.	Time hrs.	Moles H_2 per mole ester	% yield of products	
Bu oleate	86	50	Zn–Cr–O	300	11	1.86	65	octadecenol[a]
Bu oleate	129	71	Zn–Cr–O	283	11	..	63	octadecenol
Bu oleate	65	32	Zn–Cr–O	282	8	1.87	46	octadecenol
							34	octadecenyl oleate
Bu erucate	50	25	Zn–Cr–O	295	7	1.82	68	ducosenol[b]
Bu undecen-10-oate	43	21	Zn–Cr–O	293	11	1.63	37	undecenol[c]
Bu oleate	65	6.5	Cu–Cr–O	250	..	2.97	86	octadecanol
Et oleate	65	20	Zn–V–O	300	5	1.15	55	octadecenyl oleate
Et oleate	65	20	Zn–Mo–O	280	4	..	67	octadecenol and Et oleate
Et oleate	65	7.5	Cu–Mo–O	250	4	1.32	70	Et stearate
Et oleate	65	7.5	Cu–V–O	275	5	2.20	8–10	octadecanol-1
							63	octadecyl stearate
Et oleate	65	20	Zn–Cr–O	300	5	1.30	50–60	octadecenol[d]

[a] B. p. 158° (2 mm.), n^{20}D 1.4605, after refractionation 1.4579. [b] B. p. 196° (3 mm.), m. p. 34–35°. [c] B. p. 133° (16 mm.), n^{19}D 1.4500, after refractionation 1.4473, phenylurethan m. p. 54–55°. [d] Contained small amount of Et oleate.

TABLE II

ANALYSIS OF ESTERS

Name of compd.	Formula	Mol. wt.		B. p., °C.	Mm.	n^{25}D	Carbon, %		Hydrogen, %	
		Calcd.	Found				Calcd.	Found	Calcd.	Found
n-Butyl erucate	$C_{21}H_{41}CO_2C_4H_9$	394	395	211–212	1	1.4538	79.13	79.06	12.73	12.95
Octadecyl stearate	$C_{17}H_{35}CO_2C_{18}H_{37}$	536	539	M. p. 62°		....	80.52	80.55	13.51	13.71
n-Butyl undecen-10-oate	$C_{10}H_{19}CO_2C_4H_9$	240	240	116	2	1.4391	74.93	74.97	11.74	12.15
Octadecenyl oleate	$C_{17}H_{33}CO_2C_{18}H_{35}$[a]	532	539	272	1	1.4618	...	...	...	...

[a] Meyer and Lühdemann, *Helv. Chim. Acta*, **18**, 307 (1935).

such as butyl penten-4-oate and ethyl cinnamate which have their double bond near the carbalkoxy group.

The catalysts were prepared by the same general process[2] previously used. The details for preparing zinc-chromium oxide are as follows: 250 g. of ammonium dichromate (1.0 *M*) was dissolved in 600 cc. of water and concd. ammonium hydroxide added until the liquid changed from orange to yellow (400 cc. of concd. ammonium hydroxide). To this solution was added 379 g. (2.0 *M*) of zinc nitrate dissolved in 800 cc. of water. The yellow precipitate (333 g.) was filtered, washed and dried overnight in an oven at 85°. The dried precipitate was decomposed in four portions, washed in 5% acetic acid for several minutes, filtered and dried overnight in an oven at 85°. The final yield of a brown colored catalyst was 220 g.

The oleates were prepared by the alcoholysis of olive oil.[3] Butyl erucate was similarly prepared from rapeseed oil. Butyl undecen-10-oate was prepared from the acid (b. p. 141–143° at 13 mm.)[4] according to a standard method.[5] The hydrogenations were carried out at 200 atmospheres by the standard method.[6] The products were separated by fractionation. The alcohols were shown to be ester free and the yields are based upon iodine numbers for the unsaturated alcohols. The samples of octadecenol,[7] ducosenol,[7] and undecenol[8] referred to in Table I contained 13, 3 and 9%, respectively, of the corresponding saturated alcohols. The octadecenol and ducosenol were also characterized by hydrogenation to octadecanol and ducosanol, m. p. 57–58° and 69°, respectively.

Summary

It has been shown that butyl oleate or butyl erucate may be hydrogenated over zinc–chromium

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(2) Lazier, U. S. Patent 1,746,783 (1930); Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

(3) E. E. Reid, "Org. Syntheses," John Wiley and Sons, New York City, Vol. XV, 1935, p. 51.

(4) Kraft, *Ber.*, **10**, 2034 (1877).

(5) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York City, 1932, p. 256.

(6) Folkers and Adkins, THIS JOURNAL, **54**, 1145 (1932).

(7) Willstätter and Mayer, *Ber.*, **41**, 1478 (1908); Willstätter, Mayer and Hüni, *Ann.*, **378**, 101 (1911).

(8) Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 1210 (1904); Chuit, Boelsing, Hausser and Malet, *Helv. Chim. Acta*, **9**, 1074 (1926).

oxide at 300° to give the corresponding unsaturated alcohol octadecenol or ducosenol in yields of above 60%.

MADISON, WISCONSIN RECEIVED NOVEMBER 9, 1936

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

Studies on the Chemistry of the Fatty Acids. I. The Purification of Linoleic Acid by Crystallization Methods[1]

BY J. B. BROWN AND GEORGE G. STONER

On account of the recently discovered nutritional significance of linoleic acid, $C_{18}H_{32}O_2$, interest in its chemistry has increased greatly during the past few years. The acid occurs naturally in large amounts in the semi-drying oils, especially such oils as cottonseed, corn, soy bean and wheat germ. Despite several investigations on the subject there is still some question whether the acid occurs in these oils as a single geometric isomer or whether it occurs along with one or more of the other three possible forms. (We are considering here only the 9–10, 12–13, octadecadienoic acids although the possibility of other dienoic acids is not precluded.) One reason for this uncertainty is the fact that so far only one method has been available for preparing the pure acid, namely, that of Rollett.[2] In this method the mixed fatty acids of an oil are brominated in cold ether, the petroleum ether–insoluble bromides are isolated and purified and the linoleic acid is regenerated by heating with zinc dust. The product is satisfactory and is designated as α-linoleic acid.

Preparation of the acid by Rollett's method is unsatisfactory from the standpoint of yield, since in the bromination process considerable amounts of material are converted into petroleum ether-soluble isomeric bromides which are lost, and from the standpoint of chemical identity, since there is the question of alteration of the acid during bromination and debromination.

The object of the present work was to prepare linoleic acid by direct crystallization methods which did not involve bromination. As raw materials we have employed the fatty acids of refined cottonseed and corn oils containing approximately 50% of linoleic acid, the other acids present being principally palmitic and oleic.

Crystallization of cottonseed fatty acids from methyl alcohol, 95% ethyl alcohol, petroleum ether and acetone at −20° gave separations of saturated and unsaturated acids with an efficiency approaching that of the widely used lead soap–ether method. Fractional crystallization of cottonseed and corn oil fatty acids from acetone gave linoleic acid preparations 80–93% pure. The chief obstacle to the isolation of purer specimens is the fact that in attempting to obtain the more soluble constituent in every case, the product was always contaminated with oleic acid in proportion to the ratio of the solubility of linoleic acid to oleic acid under the experimental conditions. Crystallization of fatty acid mixtures at low temperatures constitutes a valuable method for the separation of these acids.

A large number of soap separations were tried. Of these, crystallization of the lithium soaps of cottonseed oil fatty acids from *n*-butanol at −20° gave 81% linoleic acid in the filtrate.

Experimental

Materials.—The sources of the fatty acids used in this work were commercial refined cottonseed and corn oils. The following analytical data were obtained on these oils.

	Cottonseed	Corn
	Original oil	
Saponification no.	194.5	194.0
Iodine no.[a]	112.0	129.9
	Fatty acids	
Mean mol. wt.	276	282.9
Iodine no.	119	133.8

[a] All iodine numbers determined by the Wijs method.

Typical analyses of these oils have shown the following fatty acid composition.

	Cottonseed[a]	Corn[b]
Linoleic	45–50	39.1
Oleic	25–30	43.4
Myristic	Small amount	. .
Palmitic	19.8	7.3

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[1] Presented at the September, 1936, meeting of the American Chemical Society.

[2] A. Rollett, *Z. physiol. Chem.*, **62**, 410 (1909).

Stearic	Small amount	3.3
Arachidic	Small amount	0.4
Lignoceric	...	.2

[a] T. P. Hilditch and J. Priestman, *Analyst*, **56**, 358 (1931). [b] G. S. Jamieson and W. F. Baughman, THIS JOURNAL, **43**, 2696 (1921).

The fatty acids were prepared by saponification and acidification. They were distilled at low pressure. Linolenic acid was shown to be absent by the hexabromide test.

Special Equipment.—Through the courtesy of Dr. F. A. Hartman of the Physiology Department we had the use of a room maintained at −20 to −25°. This room was equipped with suction for rapid filtration. For work at temperatures lower than −20° we used the following apparatus. A 200 × 200 mm. specimen jar was boxed and surrounded by rock wool insulation, with a glass plate as a cover. A circular disk was cut from this plate so that when in place it would fit loosely over a 2-liter Erlenmeyer flask, which was set in the jar on a wire tripod to raise it off the bottom. The flask was equipped with a good stirrer and a low temperature thermometer. The jar was partially filled with alcohol. Dry ice was added to the alcohol as needed. By this arrangement temperatures as low as −50 to −60° could be obtained in twenty to thirty minutes, and as low as −75° in a little longer time. This apparatus was used in the laboratory but all low temperature filtrations were carried out by suction in the −20° room in apparatus cooled to that temperature. Practically all of our crystallization mixtures filtered rapidly, so that there was very little "warming" effect before the filtration was complete.

Separation of the Saturated and Unsaturated Acids.—Four hundred and fifty grams of the cottonseed oil acids was dissolved in 4000 cc. of acetone in a 4-liter Erlenmeyer flask and allowed to stand at −20° overnight. They were filtered by suction on a large Büchner funnel previously cooled to −20° and were washed with cold acetone. Acetone was removed from both crystals and filtrate by warming under reduced pressure. The unsaturated acids were distilled before analysis; yield 140 g. of saturated acids and 300 g. of unsaturated acids. The analytical data on these preparations as well as on a number of others prepared under various experimental conditions are given in Table I.

The best separations were from 10% solutions in acetone and in methyl alcohol at −20°. Petroleum ether and ethyl alcohol were almost as efficient. Separation from solutions of higher than 10% concentration was rendered less complete due to the bulk of the precipitate, which makes filtration and washing more difficult. For best results the initial concentration of saturated acids in the acetone solution should not exceed 2.5 to 3.0%. The separation in acetone and methyl alcohol is at least as efficient as the standard lead soap–ether procedure. This is borne out by the fact that lead soaps of the unsaturated acids which were prepared by the acetone method were completely soluble in ether at room temperature, and precipitated no insoluble soaps even at ice box temperature. Further work is in progress, studying the possibility of this method as a substitute for the lead soap–ether procedure.

Assuming the unsaturated acids in experiment 4 to be a mixture of oleic and linoleic acids, and calculating from the iodine number, the mixture contains 70% linoleic acid.

Crystallization of the Unsaturated Fatty Acids of Cottonseed Oil from Organic Solvents at Low Temperatures.—The unsaturated fatty acids, prepared by the −20° treatment in acetone and containing 70% linoleic acid, were crystallized at various temperatures and concentrations from several organic solvents. From a 10% solution in toluene at −70° the acids in the filtrate contained 76% linoleic acid; from the same concentration in ether the crystals contained 53% and the acids of the filtrate 73% linoleic acid. A 10% solution in acetone crystallized at −50° gave crystals of 49% and a filtrate containing 82% linoleic; at −60 and at −70° the separation was less satisfactory, the acids of the filtrate being 78 and 76% linoleic, respectively. A 1% solution in acetone crystallized at −65° gave 79% linoleic acid in the filtrate. Of these data the −50° crystallization in acetone is the most promising. This favorable result is no doubt due in part to removal of further traces of saturated acids which remained unavoidably in the unsaturated acids and in part to the crystallization of an oleic acid rich fraction.

Fractional Crystallization of the Unsaturated Acids.—In order to study further crystallization in certain solvents at various low temperatures, the unsaturated acids of cottonseed oil were fractionally crystallized from methyl alcohol, acetone, ethyl alcohol and 76% acetone. The solution was cooled to a given temperature with fairly rapid

TABLE I

SEPARATION OF SATURATED AND UNSATURATED ACIDS

				Satd. fatty acids (Not distilled)		Unsatd. acids (Distilled)	
Expt.	Solvent	Concn. of acids, g./100 cc.	Temp., °C.	Iod. no.	Mean mol. wt.	Iod. no.	Mean mol. wt.
1	Acetone	12	0	None		....	..
2	Acetone	18	−20	Not determined		153.4	279
3	Acetone	12	−20	33.0	263	154.9	280
4	Acetone	10	−20	7.2	258	153.7	280
5	Petroleum ether	10	−20	5.6	267	151.5	..
6	Alcohol (95%)	10	−20	12.6	264	152.5	..
7	Methyl alcohol	12	0	4.1	263	140.2	280
8	Methyl alcohol	12	−20	3.4	...	149.2[a]	280[a]
9	Methyl alcohol	10	−20	5.8	260	154.4[a]	282[a]

[a] Saponified before analysis to remove any esters which might have been formed.

TABLE II

FRACTIONAL CRYSTALLIZATION OF THE UNSATURATED ACIDS OF COTTONSEED OIL

Solvents	Concn. in solvents, %	Temp., °C.	% total wt.	Iodine number	% linoleic
Methyl alcohol	10	Ppt. −50	25	134.8	50
		Ppt. −55	16	159.2	74
		Ppt. −60	28	157.7	75
		Ppt. −65	15	168.2[a]	86
		Filtrate −65	16	156.5	73
Acetone	13	Ppt. −45	29	128.0	42
		Ppt. −50	16	155.0	72
		Ppt. −55	26	159.0	76
		Ppt. −60	9	167.8[a]	85
		Filtrate −60	20	153.4	70
Alcohol	10	Ppt. −50	44	151.6	68
		Ppt. −60	26	160.6	78
		Ppt. −70	13	161.8	79
		Filtrate −70	17	149.6	65
Acetone 76% by volume	7	Ppt. −40	29	111.0[a]	23
		Ppt. −70	46	160.0[a]	77
		Filtrate −70	25	163.3	81

[a] These specimens were distilled before the iodine number was determined.

stirring. It was filtered rapidly in the −20° room; the filtrate was then cooled further, this process being repeated, as shown in Table II.

The precipitate from methyl alcohol at −65°, *i. e.*, that portion of the total acids which came down by cooling a solution, saturated at −60, to −65° contained 86% linoleic acid; that precipitated at −60° from acetone contained 85% of the desired product. These represent the best products we have been able to obtain from cottonseed oil, but they constitute too small a part of the total acids to be of great value. It should be noted especially that in each instance maximum removal of unwanted acids (product of low iodine number) occurred in the first crop of crystals.

In order to take advantage of this fact the following procedure was carried out. Two thousand grams of refined cottonseed oil was saponified and converted into fatty acids. Four hundred and fifty grams of these acids was placed in a 4-liter Erlenmeyer flask and the flask filled with acetone. After standing overnight at −20°, the contents of the flask were filtered with suction. Four such lots were run (1800 g.), the total filtrate being 12 liters. In batches of 2 liters this filtrate was cooled to −40°, which was slightly below the point of initial appearance of crystals. The crystals were filtered off; the resulting filtrate from the entire lot contained 1010 g. of acids with an iodine number of 160 (77% linoleic acid).

Fractional Crystallization of the Unsaturated Methyl Esters from Methyl Alcohol.—Methyl esters (iodine number 152) were prepared from the unsaturated acids previously described. These esters were fractionally crystallized from a 12% solution in methyl alcohol, successive crops of crystals being removed at −45, −65 and −75°. The iodine numbers of the esters of these products and of the esters in the filtrate were 56.7, 142.3, 156.1 and 147.4, respectively, the yields, calculated as percentage total weight of ester used, were 2, 58, 32 and 8, respectively. The crystals at −75° contained approximately 82% methyl linoleate. Undoubtedly this procedure offers possibilities, but, so far, we have not studied it further.

Fractional Crystallization of Corn Oil Fatty Acids.—The unsaturated fatty acids of corn oil were prepared by the −20° acetone procedure; these were fractionally crystallized from this solvent under a variety of conditions. The details and results are shown in Table III.

We have succeeded here in obtaining satisfactory yields of linoleic acid 85, 86 and 88% pure, and less satisfactory yields of the acid 89 and 93% pure. It is possible then to prepare the acid by these latter procedures in sufficient purity for most chemical studies. We hope to have available shortly data comparing the acid which has been purified in this manner with α-linoleic acid prepared by Rollett's procedure.

Attempts to Purify Linoleic Acid by Crystallization of the Soaps of the Fatty Acids of Cottonseed Oil.—Several

TABLE III

CRYSTALLIZATION OF CORN OIL FATTY ACIDS[a]

Description	Wt. acids used. g.	Vol.	Yield, g.	Mean mol. wt.	Iod. no.	% linoleic
Filtrate at −55°	360	4000	78	...	167.1	85
−55 to −70° fraction of unsatd. acids[b]	320	4000	40	...	171.3	89
Acids, −45 to −70°	150	2000	95	279.6	168.5	86
Acids, −50 to −70°	150	2000	75	279.3	170.2	88
Filtrate (−70°) cooled to −80°; crystals rejected		1700	15	281.3	174.6	93

[a] Iodine no. of corn oil unsatd. acids, 156 (72.5% linoleic). [b] The −55 to −70° fraction was crystallized from 1 liter of acetone at −75°. Data above are on the crystals.

Table IV

Fractional Crystallization of Lithium and Potassium Soaps

Soap	Solvent	Temp., °C.	% total wt.	Iod. no.	% linoleic
Lithium	Butyl alcohol	Ppt. 30	3	...	..
		Ppt. 0	41	82.4	..
		Ppt. −20	41	144.0	60
		Filtrate −20	15	164.5	82
Potassium	Ethyl alcohol	Ppt. 30	1	...	..
		Ppt. 0	34	49.2	..
		Ppt. −20	26	134.8	49
		Filtrate −20	39	157.8	74.3

of the more useful methods of fatty acid separation involve differences of soap solubility. Early in this work we were hopeful of finding some suitable soaps of oleic and linoleic acids which would exhibit wide enough difference in solubility to be useful in their separation. Only a few of our more promising results will be reported here. Starting with cottonseed oil fatty acids, crystallization of the potassium soaps from a 10% solution in absolute alcohol at 0° gave 45% insoluble soaps and 55% soluble soaps, containing 68% linoleic acid. The lithium soaps, prepared by neutralizing a solution of the acids in alcohol with lithium hydroxide, removing the alcohol and water under reduced pressure and taking up the soaps in butyl alcohol, were fractionally crystallized from that solvent; also the potassium soaps from absolute alcohol with the results in Table IV.

When the fact is considered that we began here with a mixture of cottonseed oil fatty acids, it is clear that either of the separations in Table IV has possibilities. In the former case, a comparatively small amount of the acids comes out as 82% linoleic, while in the latter a much larger portion came out 74% linoleic acid.

Summary

1. The saturated and unsaturated fatty acids of cottonseed and corn oils may be separated conveniently by crystallization of the mixed acids from a 10% solution in acetone at −20°.
2. Linoleic acid preparations containing up to 93% of the acid were obtained by fractional crystallization of the unsaturated acids (and methyl esters) of these oils from acetone and methyl alcohol at low temperatures.
3. Fractional crystallization of the lithium soaps from *n*-butyl alcohol and of the potassium soaps from absolute alcohol may also be used in obtaining linoleic acid concentrates.
4. Crystallization of unsaturated fatty acids from appropriate solvents at low temperatures is a useful procedure for their separation.

Columbus, Ohio Received October 3, 1936

[Contribution from the Laboratory of Physiological Chemistry, The Ohio State University]

Studies on the Chemistry of the Fatty Acids. II. The Preparation of Pure Oleic Acid by a Simplified Method[1]

By J. B. Brown and G. Y. Shinowara

Although oleic acid (*cis*-9,10-octadecenoic) is perhaps the most common of the naturally occurring fatty acids, the pure acid is still one of the rare chemicals. The reason for this state of affairs is that oleic acid always occurs in fats and oils associated with saturated acids and usually with varying amounts of linoleic acid and other acids of higher unsaturation. The methods for separating these impurities are only semi-quantitative so that purification of oleic acid is extremely tedious. Olive oil is usually employed as a source of the acid. The saturated acids, mostly palmitic, are removed by the lead soap separation in alcohol or ether; the unsaturated acids are then converted into barium soaps which are repeatedly crystallized from moist benzene to remove linoleic acids.

Excellent reviews of work previous to 1925 are given by Lewkowitsch[2] and by Lapworth, Pearson and Mottram.[3]

These investigators prepared the pure acid by a procedure which included the lead salt treatment, distillation, barium soap crystallization and finally distillation. Holde and Gorgas[4] claimed

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(1) Presented at the Pittsburgh Meeting of the American Chemical Society, September, 1936.

(2) J. Lewkowitsch, "Technology of Oils, Fats and Waxes," Macmillan and Co., Ltd., London, Vol. I, 1921, p. 182.

(3) A. Lapworth, L. K. Pearson and E. N. Mottram, *Biochem. J.*, **19**, 7 (1925).

(4) D. Holde and A. Gorgas, *Z. angew. Chem.*, **39**, 1443 (1926).

the preparation of a pure product through reduction of dibromostearic acid. Bertram[5] prepared 99.5% oleic acid by use of the Twitchell[6] lead salt–alcohol procedure, formation of the silver salt and crystallization of the acid three times from acetone. Raymond[7] modified the Bertram method by eliminating the use of a silver salt, and crystallizing the acid from cold alcohol in a special apparatus. Shelton[8] likewise used the Twitchell separation and in addition crystallized the barium or lithium salts and distilled the methyl esters of the resulting product.

All procedures so far used that have resulted in satisfactory products have been tedious and have employed a combination of methods to attain the desired results. As a result of experience gained in the course of the preceding work[9] it seemed likely that we could obtain oleic acid of a high degree of purity by direct crystallization of the acids of olive oil from acetone. Our method in brief involves removal of the saturated acids by the −20° acetone precipitation, crystallization of the resultant unsaturated acids from acetone at −60° four or more times, followed by a partial crystallization of the resultant product from acetone at −35° to remove small amounts of palmitic acid not taken out by the original treatment at −20°. Three preparations are described and compared with other preparations reported in the literature. The multifarious operations of previously reported methods are replaced by seven or more crystallizations from the same solvent. No soap preparations are involved after the original saponification.

Experimental Part

Equipment.—For low temperature work we had available the special equipment described previously, namely, a room in which a temperature of −20 to −25° was maintained and a well insulated dry ice–alcohol apparatus designed to accommodate a 2-liter Erlenmeyer flask. All filtrations were carried out by suction in the −20° room.

Procedures.—(1) One kilogram of olive oil (iodine number 85.5; saponification number, 190.1) was saponified and the soaps converted into fatty acids (iodine number 84.5). Two hundred and twenty-five grams of the acids was dissolved in 3450 cc. of C. P. acetone in a 4-liter flask and allowed to stand in the cold room overnight. The precipitate was removed by suction on a large Büchner funnel. The filtrate (3000 cc.) was cooled to −60° with continuous stirring. After filtering, the precipitate was allowed to melt and was made up to 2000 cc. with acetone, and again brought to −60° and filtered. After two more crystallizations at this temperature, the final precipitate was melted and made up to 1250 cc. with acetone and cooled slowly with stirring to the point of first appearance of crystals, about −35°. These, consisting of some oleic acid and any saturated acids which may have escaped the first crystallization, were filtered off in the cold room. The acetone was removed from the filtrate by warming under reduced pressure. The residual product was distilled at 15 mm. pressure in an entire glass apparatus. It was water-white and odorless; yield 90 g. Other constants are in Table I.

TABLE I

ANALYSIS OF OLEIC ACID PREPARATIONS IN COMPARISON WITH THOSE REPORTED IN THE LITERATURE

	M.p., °C.	Mean mol. wt.	Iodine number	n^{20}	Purity, %
Calcd.	...	282.3	89.93	....	
Specimen (1)	13.0	282.2	90.03	1.4585	
Specimen (2)	13.0	282.4	89.63	1.4586	
Specimen (3)	13.0	282.5	90.04	1.4585	
Bertram	13.2	...	...	1.4582	99.5
Shelton	13–14	282.5	90.6	1.4610	

(2) Four hundred and fifty grams of the mixed acids, as above, was treated as before, except that six −60° crystallizations, instead of four, were made; yield 135 g.

(3) The −60° filtrates from the two preceding experiments were combined; the acetone was removed. Two hundred and fifty grams of these acids was made up to 1500 cc. in acetone and crystallized four times at −60°; crystals were washed each time with 200 cc. of acetone cooled to −70°; yield 74 g.

All three of these preparations were practically constant boiling. The boiling point of No. 2 oleic acid was determined accurately at several pressures, using a micro-gage with the following results.

Pressure	B. p., °C. Obsd.	Corr.
15	228–229	234–235
10	219–220	225–226
5	209–210	215–216
1.2	194–195	200–201

Criteria of Purity.—We have employed the following criteria of purity, actual data being given in Table I. (1) Mean molecular weight: The principal saturated acid of olive oil is palmitic. Five per cent. contamination with this acid would lower this value 1.4 points. No appreciable lowering was observed. (2) Iodine number: Method used, Wijs thirty minutes. Palmitic and linoleic acids must be present in equal amounts to maintain the theoretical value. (3) Melting point: Specimens, frozen in a special tube and held overnight. All three preparations melted sharply at 13°. Difference between softening and melting point was less than 0.1°. (4) Oxidation products: Dihydroxystearic acids were prepared from each product by the method of Lapworth and Mottram;[10] yield, 95–96%; molecular weight 315.6–316.0 (calcd. 316.3).

The data are summarized in Table I.

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(5) S. H. Bertram, *Rec. trav. chim.*, **46**, 397 (1927).

(6) E. Twitchell, *J. Ind. Eng. Chem.*, **13**, 806 (1921).

(7) E. Raymond, *Chimie et Industrie*, Feb., 523 (1929).

(8) J. H. Shelton, *J. Soc. Chem. Ind.*, **50T**, 131 (1931).

(9) J. B. Brown and G. G. Stoner, THIS JOURNAL, **58**, 3 (1936).

(10) A. Lapworth and E. N. Mottram, *J. Chem. Soc.*, 1628 (1925).

Summary

1. A simplified procedure for preparing oleic acid of high purity is described.

2. The constants of three specimens of oleic acid, prepared by slight modifications of the procedure, are described.

COLUMBUS, OHIO RECEIVED OCTOBER 3, 1936

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

A Method for the Synthesis of Phenanthridine Derivatives by an Application of the Stieglitz Rearrangement

BY LOUIS A. PINCK AND GUIDO E. HILBERT

The rearrangements of hypothetical intermediates $\left.\begin{matrix}R_1\diagdown\\R_2-\\R_3\diagup\end{matrix}\right. C-N:$ resulting from appropriate treatment of tertiary methyl nitrogen substituted compounds of the type $\left.\begin{matrix}R_1\diagdown\\R_2-\\R_3\diagup\end{matrix}\right. C-N\left\langle\begin{matrix}X\\Y\end{matrix}\right.$ where R$_1$, R$_2$ and R$_3$ usually have been aromatic groups and where $-N\left\langle\begin{matrix}X\\Y\end{matrix}\right.$ may be $-N\left\langle\begin{matrix}H\\Br\end{matrix}\right.$,[1] $-N\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.$,[1] $-N\left\langle\begin{matrix}H\\OH\end{matrix}\right.$,[2] —N(N$_2$),[3] etc.,[4] have been studied extensively by Stieglitz and co-workers.[5] When R$_1$ is aliphatic in nature and R$_2$ and R$_3$ are aromatic, it was noted that either R$_2$ or R$_3$ rather than R$_1$ migrated to the nitrogen atom and largely on the basis of this fact it has been suggested[5] that the migration of the most electronegative group attached to the carbon atom would in general be favored. The rearrangement of intermediates formed from tertiary methyl nitrogen derivatives, where two of the groups attached to the tertiary carbon atom are linked together, as for example in a 9-substituted 9-fluorylchloroamine (II), has not previously been studied. Here the situation is more complicated, since the possible influence that the five-membered ring might have on the rearrangement must be considered in addition to the electronegativities of the radicals. From the general results of recent x-ray and electron diffraction studies[6] fluorene would be expected to have the configuration shown in Fig. 1.[7] In order that the C–C distances be those shown in the figure the normal valence angle from the benzene ring must be distorted approximately 12 to 13°. Since the linkages attached to the benzene ring are known to be quite rigid the five-membered ring in fluorene, because of the considerable distortion of the normal valence angles, must be appreciably strained. Theoretically a 9-substituted fluoryl nitrogen (III) can be stabilized by undergoing two possible types of rearrangement: (1) opening of

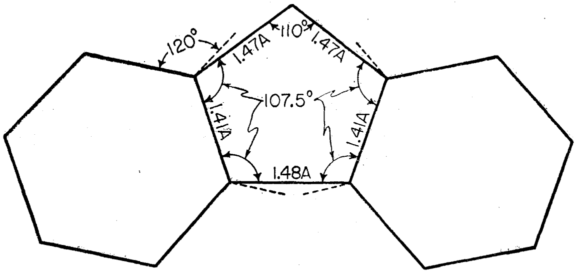
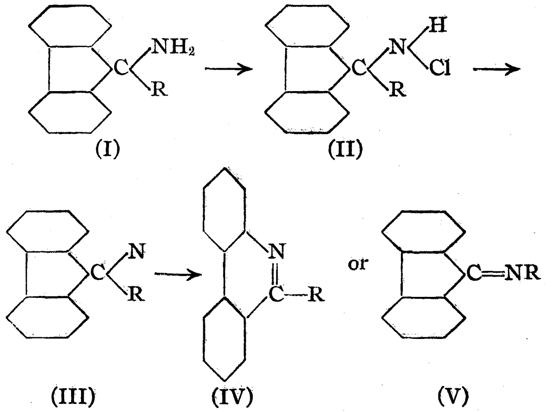


Fig. 1.—Structural formula of fluorene.



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[1] Vosburgh, THIS JOURNAL, **38**, 2081 (1916).

[2] Stieglitz and Leech, *ibid.*, **36**, 272 (1914).

[3] Senior, *ibid.*, **38**, 2718 (1916).

[4] Stieglitz and Stagner, *ibid.*, **38**, 2046 (1916); Stieglitz and Senior, *ibid.*, **38**, 2727 (1916); Guthmann and Stieglitz, *J. Org. Chem.*, **1**, 31 (1936).

[5] For a review, which also includes unpublished results, see Porter, "Molecular Rearrangements," Chemical Catalog Co., Inc., New York, 1928, pp. 30–33.

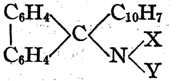
[6] Robertson, *Chem. Rev.*, **16**, 417 (1935); Hendricks, *ibid.*, **7**, 341 (1930).

[7] Stuart "Molekülstruktur," Verlag von Julius Springer, Berlin, 1934, p. 76, has interpreted the results obtained in an x-ray examination of fluorene by Hengstenberg and Mark, *Z. Krist.*, **70**, 283 (1929), as favoring a planar configuration of the molecule. Since this manuscript was written, additional articles on the configuration of fluorene have appeared. Cook and Iball, *Chemistry and Industry*, **55**, 467 (1936), on the basis of crystallographic data consider it to be a non-planar molecule, whereas dipole moment measurements by Hughes, LeFevre and LeFevre, *ibid.*, **55**, 545 and 561 (1936), suggest that fluorene is a flat molecule.

the ring with subsequent reformation to give a phenanthridine derivative (IV) or (2) migration of R to form an imide (V). As will be shown below even when R is more electronegative than the phenylene radical the rearrangement involves primarily the formation of (IV). Thus it follows that the strained condition of the five-membered ring is an important factor, if not the most important one, in directing the course of the rearrangement.

In order that the electronegativities of R in (I) be widely different, both 9-aryl- and 9-alkyl-9-fluorylamines were investigated. Examples chosen as being representative of the two types were the 9-phenyl- (VI), 9-(α-naphthyl) (VII) and 9-methyl-9-fluorylamines (VIII). Although the first two were prepared smoothly by treating the corresponding 9-chloro compounds with ammonia, considerable trouble was encountered in preparing the 9-methyl derivative. A solution of ammonia in toluene gave with 9-bromo-9-methylfluorene, a mixture of amines, consisting of (VIII), an isomer, probably 9-fluorylmethylamine, and a secondary amine, as well as an appreciable amount of polymerized biphenyleneethylene.[8] The difficulty in this case is to be attributed to the relatively labile hydrogen of the neighboring methyl group. It is of interest that a number of these amine hydrochlorides are soluble in benzene and chloroform and that practically all have an anesthetic action on the tongue.[9]

Interaction of hypochlorous acid with alcoholic solutions of (VI), (VII) and (VIII) gave the corresponding chloroamines. The hydrogen and chlorine atoms attached to the nitrogen were most conveniently removed by treating the chloroamine in anhydrous pyridine with sodium methylate at room temperature. Of some significance in possibly offering a clue as to the nature of the intermediate formed in the reaction may be the color changes exhibited by the reaction mixture. During the degradation of 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine a red color developed in the solution and persisted for a short time; however, in the case of the 9-methyl analog the color remained over a period of twelve hours. The rearrangement products formed from 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine are 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-phenanthridine, respectively. In every case the yield was excellent. The structures of 9-methyl- and 9-phenylphenanthridine were established by comparison of these compounds with authentic specimens prepared from acetyl- and benzoyl-*o*-xenylamine according to the method of Morgan and Walls.[10] If the formation of the rearranged compound had been controlled only by a shift of the most electronegative group attached to the tertiary carbon atom, the predicted[11] products from 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine would have been 9-methylphenanthridine, 9-phenyliminofluorene (V where R = C_6H_5) and 9-(α-naphthyl)-iminofluorene (V where R = $C_{10}H_9$). Actually, imino compounds, which could have been easily detected even if formed in minor amounts, were found to be absent.

In order to find if other compounds of the type  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}C_{10}H_7\\ N\!<\!\!\begin{matrix}X\\ Y\end{matrix}\end{matrix}$ could be converted into derivatives of phenanthridine an investigation of the thermal decomposition of 9-(α-naphthyl)-9-fluorylazide was carried out. 9-(α-Naphthyl)-9-fluorylhydrazine (IX) was prepared by the interaction of 9-(α-naphthyl)-9-chlorofluorene with hydrazine. The reaction was not smooth and owing to its lability the hydrazine derivative was difficult to obtain in the pure state. Nitrous acid with (IX) gave the azide. This when heated to 190–200° evolved nitrogen and formed 9-(α-naphthyl)-phenanthridine in good yield. Because of the difficulty encountered in dealing with (IX), the phenanthridine derivatives are much more conveniently prepared by way of the chloroamines.

The compounds to which the Stieglitz rearrangement has been applied in the past yield imides as the end-products of the reaction. Since these are much more easily prepared by other methods the rearrangement was chiefly of theoretical interest. In view of the present work it appears that this rearrangement may also assume considerable practical importance as a method for converting suitable five-membered cyclic compounds to six-membered nitrogen rings.

We are grateful to Mrs. M. S. Sherman for carrying out the analyses recorded in the experimental work.

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[8] Wieland, Reindel and Ferrer, *Ber.*, **55**, 3313 (1922).

[9] Nakamura, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **14**, 184 (1930), reported the local anesthetic action of 9-fluorylamine hydrochloride.

[10] Morgan and Walls, *J. Chem. Soc.*, 2447 (1931).

[11] From a comparison of the reactivities of diphenylmethyl with biphenylenemethyl derivatives or of triphenylmethyl with phenylfluoryl derivatives, the phenyl group would be expected to be more electronegative than the phenylene radical.

Experimental

9-Phenyl-9-fluorylamine, its Derivatives and its Conversion to 9-Phenylphenanthridine

9-Phenyl-9-fluorylamine.—A mixture of 10 g. of 9-phenyl-9-chlorofluorene and about 15 cc. of liquid ammonia was heated in a sealed tube at 60° for several hours.[12] An oil separated and upon evaporation of the ammonia a sirupy residue remained. Owing to its marked sluggishness in crystallizing, the amine was purified only with difficulty by numerous crystallizations from either petroleum ether or 75% ethyl alcohol. It separated as colorless prisms melting at 82°[13] and was very soluble in most organic solvents.

Anal. Calcd. for $C_{19}H_{15}N$: C, 88.67; H, 5.88; N, 5.45. Found: C, 88.85; H, 6.15; N, 5.47.

9-Phenyl-9-fluorylamine was not hydrolyzed when heated at 100° for one hour with 20% hydrochloric acid, whereas under similar conditions triphenylmethylamine yielded an appreciable amount of the carbinol. The amine was also recovered unchanged after treatment with a solution of potassium permanganate in purified acetone in the presence of anhydrous sodium sulfate[14] for several days at room temperature. The stability of 9-phenyl-9-fluorylamine toward oxidizing agents is further shown by its recovery after refluxing for two hours an alcoholic solution to which had been added bromine and sodium ethylate.[15]

The hydrochloride was prepared by passing dry hydrogen chloride into a benzene solution of the amine; it crystallized from dilute hydrochloric acid as microscopic prisms melting at 310° with decomposition.

Anal. Calcd. for $C_{19}H_{15}N{\cdot}HCl$: C, 77.66; H, 5.49; N, 4.88. Found: C, 78.00; H, 5.32; N, 4.93.

The acetyl derivative was secured in the usual manner and crystallized from alcohol as microscopic prisms, m. p. 232°.

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.24; H, 5.72; N, 4.68. Found: C, 83.79; H, 5.92; N, 4.65.

The monobromoamine was prepared according to the method of Vosburgh.[1] The amounts of reagents used were 2.60 g. of 9-phenyl-9-fluorylamine, 1.62 g. of bromine, and 3.22 cc. of an aqueous solution containing 0.41 g. of sodium hydroxide. The chloroform solution was concentrated and the sirupy residue dissolved in 30 cc. of warm, low-boiling ligroin. Upon cooling a pale yellow microcrystalline material separated; yield 1.60 g. After recrystallization it melted at 105° (dec.).

Anal. Calcd. for $C_{19}H_{14}NBr$: Br, 23.78. Found: Br, 24.09.[16]

The monochloroamine was prepared by using a method similar to that of Hellerman and Sanders.[17] A solution of 2.72 g. of 9-phenyl-9-fluorylamine hydrochloride in 75 cc. of 95% ethyl alcohol[18] was treated at 0° with 10 cc. of cold 0.926 *N* potassium hypochlorite. Minute colorless crystals immediately precipitated. The reaction mixture was shaken in an ice-bath for thirty minutes and cold water added to ensure complete precipitation. The colorless solid was collected, washed with cold water and dried *in vacuo* over phosphorus pentoxide; yield, practically quantitative. The monochloroamine separates from hexane as colorless prisms; m. p. 102°.

Anal. Calcd. for $C_{19}H_{14}NCl$: C, 78.20; H, 4.84; N, 4.80; Cl, 12.16. Found: C, 77.68; H, 4.84; N, 4.58; Cl, 12.21.

The dichloroamine was synthesized by passing an excess of chlorine into an alcoholic solution of 9-phenyl-9-fluorylamine. It was obtained in good yield and after crystallizing from ligroin melted at 150° (dec.). This material is unusually stable and may be kept for several years without any apparent alteration.

Anal. Calcd. for $C_{19}H_{13}NCl_2$: C, 69.94; H, 4.02; N, 4.30; Cl, 21.75. Found: C, 70.09; H, 4.43; N, 4.35; Cl, 20.33.

Di-(9-phenyl-9-fluoryl)-amine was obtained as a by-product in the following experiment. Forty grams of 9-phenyl-9-chlorofluorene and a large excess of dry ammonia were heated in a steel bomb at 180° for four hours. The reaction product, after evaporation of the ammonia, was triturated with 100 cc. of alcohol[19] and the residue extracted with toluene. The hot toluene filtrate was treated with an equal volume of hot alcohol and on cooling the secondary amine separated. Several crystallizations from a solution of alcohol and toluene gave 3 g. of glistening, elongated, hexagonal plates, m. p. 230°.

Anal. Calcd. for $C_{38}H_{27}N$: C, 91.71; H, 5.47; N, 2.82. Found: C, 91.89; H, 5.62; N, 2.90.

Conversion of 9-Phenyl-9-fluorylchloroamine to 9-Phenylphenanthridine.—A solution of 2 g. of the chloroamine in 20 cc. of anhydrous pyridine[20] was treated with

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(12) 9-Phenyl-9-chlorofluorene is much less reactive toward ammonia than triphenylmethyl chloride. Considerable heat was generated when the latter was treated with liquid ammonia at room temperature. Upon slow cooling beautiful crystals of triphenylmethylamine separated; from the interaction between 10 g. of triphenylmethyl chloride and 15 cc. of liquid ammonia 9.3 g. of the amine was isolated. Triphenylmethylamine was recovered unchanged after being subjected to a solution of ammonium chloride in ammonia for several days at room temperature. Evidently the equilibrium is shifted to a remarkable extent by an appreciable temperature change as Kraus and Rosen, THIS JOURNAL, **47**, 2739 (1925), reported that at the temperature of liquid ammonia: (1) triphenylmethyl chloride was ammonolyzed to the amine only to a slight extent and (2) the amine was converted to triphenylmethyl chloride by ammonium chloride.

(13) All melting points are corrected.

(14) Goldschmidt and Beuschel [*Ann.*, **447**, 197 (1926)] used similar conditions in dehydrogenating 9-fluorylamine to 9-iminofluorene.

(15) These conditions were used by Hellerman and Sanders, THIS JOURNAL, **49**, 1745 (1927), to dehydrogenate diphenylmethylamine.

(16) The compounds containing active halogen were analyzed by titrating in chloroformic solution against a standardized solution of sodium thiosulfate in the presence of hydriodic acid.

(17) Hellerman and Sanders, THIS JOURNAL, **49**, 1745 (1927), and private communications from Dr. Hellerman which have facilitated the work immensely.

(18) Water is usually used as the medium for the preparation of the monochloroamines. However, when water was used in the above halogenation, the reaction product was always contaminated with some unchanged amine. The use of alcohol, in which the amine hydrochloride was appreciably soluble, overcame this difficulty.

(19) From the alcoholic extract after suitable manipulation, 24.5 g. of pure 9-phenyl-9-fluorylamine hydrochloride was obtained.

(20) Absolute alcohol as a solvent resulted in the formation of the amine.

an excess of dry sodium methylate.[21] Considerable heat was generated and the solution developed a light red color which persisted for several minutes and then changed to a straw yellow. After standing overnight the pyridine was distilled from the reaction mixture under diminished pressure, the residue triturated with dry ether and the resulting extract treated with dry hydrogen chloride in order to precipitate the base as the salt. The hydrochloride was exceedingly soluble in water and crystallized as straw colored needles containing water of crystallization; m. p. 95–100° and 226°.[22] 9-Phenylphenanthridine was regenerated from the salt and crystallized from petroleum ether; colorless glistening plates, m. p. 107–108°.

Anal. Calcd. for $C_{19}H_{13}N$: C, 89.38; H, 5.13; N, 5.49. Found: C, 89.53; H, 5.36; N (Dumas), 5.48.

Comparison of its properties with those of a specimen synthesized according to the method of Morgan and Walls[10] showed them to be identical; a melting point of the mixture was not depressed.

9-(α-Naphthyl)-phenanthridine

9-(α-Naphthyl)-9-fluorylamine was prepared by heating 9-(α-naphthyl)-9-chlorofluorene (36 g.)[23] with dry ammonia in a steel bomb at 80° for forty hours. The ammonia was evaporated and the amine separated from the residue by dissolving in boiling benzene. After decolorizing with charcoal and numerous recrystallizations from solutions of benzene and alcohol, the amine melted at 186°; colorless prisms; yield 13.4 g.

Anal. Calcd. for $C_{23}H_{17}N$: C, 89.86; H, 5.58; N, 4.56. Found: C, 89.92; H, 5.66; N, 4.52.

The hydrochloride was soluble in benzene; m. p. 271° (dec.).

Anal. Calcd. for $C_{23}H_{17}N \cdot HCl$: N, 4.1. Found: N, 3.9.

The chloroamine was obtained in a practically quantitative yield and separated from a solution of benzene and hexane as beautiful colorless prisms; m. p. 133–135° (dec.).

Anal. Calcd. for $C_{23}H_{16}NCl$: C, 80.80; H, 4.72; N, 4.10; Cl, 10.38. Found: C, 81.11; H, 5.03; N, 3.91; Cl, 10.00.

9-(α-Naphthyl)-phenanthridine was prepared from 9-(α-naphthyl)-9-fluorylchloroamine (1.5 g.) in the same manner as that described for the phenyl analog. The reaction mixture in this case was not as highly colored. After removal of the volatile matter, the phenanthridine derivative was extracted with ether. It crystallized from petroleum ether in clusters of irregularly shaped colorless crystals; yield 1.1 g.; m. p. 123.5°.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.45; H, 4.96; N, 4.59. Found: C, 90.37; H, 5.08; N (Dumas), 4.59.

The hydrochloride crystallized from boiling water as cream colored needles with water of crystallization melting at 120–125°; the anhydrous product melted at 224° (dec.).

Anal. Calcd. for $C_{23}H_{15}N \cdot HCl$: C, 80.80; H, 4.72; N, 4.10. Found: C, 80.97; H, 5.10; N, 3.99.

The picrate was prepared in and recrystallized from alcohol; yellow prisms; m. p. 251°.

Anal. Calcd. for $C_{29}H_{18}N_4O_7$: C, 65.15; H, 3.40. Found: C, 65.43; H, 3.58.

9-Methyl-9-fluorylamine and 9-Methylphenanthridine

Interaction of 9-Methyl-9-bromofluorene with Ammonia.—A solution of 37 g. of 9-methyl-9-bromofluorene[9] in 30 cc. of dry toluene and 30 g. of liquid ammonia was heated in a steel bomb at 75° for twenty hours. After removing the ammonia, the insoluble fraction was collected, thoroughly washed with 150 cc. of toluene, and identified as the polymeric form of biphenyleneethylene; wt. 6.9 g.; m. p. 270°.[8]

Anal. Calcd. for $(C_{14}H_{10})_x$: C, 94.34; H, 5.66. Found: C, 93.94; H, 5.84.

The filtrate and washings were combined and acidified with an alcoholic solution of hydrogen chloride. On heating, the slight precipitate that formed dissolved and the hot solution was concentrated at reduced pressure. Fractionation of the resulting residue was effected by extraction with water; further manipulation of the aqueous insoluble portion (A) is described below. The aqueous extract was concentrated to about 75 cc. and treated with an equal volume of hydrochloric acid. Upon cooling the hot solution a mixture of colorless crystalline amine hydrochlorides (9.5 g.) separated. Efforts to resolve the mixture into its components by repeated crystallization from water failed. Advantage was taken of the differential solubility of the two amine hydrochlorides in chloroform; 9-methyl-9-fluorylamine hydrochloride was quite soluble in contrast to the other amine hydrochloride which was practically insoluble. To the chloroformic extract of the mixture was added benzene; beautiful needles separated; m. p. 266° (dec.).

Anal. Calcd. for $C_{14}H_{13}N \cdot HCl$: C, 72.55; H, 6.09; N, 6.05. Found: C, 72.62; H, 6.12; N, 5.83.

This salt was decomposed in the usual manner to liberate the free base. **9-Methyl-9-fluorylamine** was recrystallized from ligroin and separated as colorless needles melting at 96°.

Anal. Calcd. for $C_{14}H_{13}N$: C, 86.11; H, 6.71; N, 7.18. Found: C, 86.19; H, 6.80; N, 7.22.

On interacting with nitrous acid, 9-methyl-9-fluorenol was formed in good yield; m. p. and mixed m. p. 176°.

The chloroformic insoluble hydrochloride (*ca.* 1.0 g.) was crystallized from dilute hydrochloric acid; irregular

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(21) 9-Phenylphenanthridine was also prepared by treating 9-phenyl-9-fluorylbromoamine in ether with freshly precipitated silver oxide [Willstätter and Müller, *Ber.*, **41**, 2580 (1908)] in the presence of preheated sodium sulfate. Under these conditions the reaction, probably because some amine is regenerated, was not as smooth as the above, since numerous recrystallizations were required to purify the phenanthridine derivative.

(22) Pictet and Hubert [*ibid.*, **29**, 1182 (1896)] reported it to melt at 95–96 and 220°.

(23) In working up 9-α-naphthyl-9-fluorenol prepared by a Grignard reaction [Wanscheidt and Moldavski, *ibid.*, **63**, 1362 (1930)] it was noticed that the unchanged fluorenone combined with the fluorenol derivative to form a relatively stable deep yellow crystalline molecular compound melting at 109–110°. This view regarding the nature of the product was confirmed by preparing it from an alcoholic solution containing equimolal amounts of fluorenone and 9-(α-naphthyl)-9-fluorenol. Schlenk and Herzenstein, *Ann.*, **372**, 27 (1910), reported the formation of a similar type of compound between fluorenone and 9-*p*-diphenyl-9-fluorenol.

shaped crystals with marked twinning in the form of crosses; m. p. 294° (dec.).

Anal. Calcd. for $C_{14}H_{13}N \cdot HCl$: C, 72.55; H, 6.09; N, 6.05. Found: C, 72.79; H, 6.24; N, 5.96.

The free base, which is considered to be **9-fluorylmethylamine,** was prepared from the salt and crystallized from ether as colorless needles melting at 99–100°; when mixed with 9-methyl-9-fluorylamine the melting point was depressed considerably. There was insufficient material for further purification and for analysis.

The aqueous insoluble fraction (A) was triturated with benzene and from this benzene extract there was recovered 0.9 g. of a colorless crystalline hydrochloride; m. p. 263–265° (dec.). Treatment of the salt with liquid ammonia gave the free base, which was recrystallized from a solution of 20% benzene and 80% alcohol; colorless prisms; m. p. 166°.

Anal. Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.19; H, 6.44; N, 3.67.

This analysis agrees with that required for a disubstituted amine. Of the number of secondary amines possible, that which seems to agree best with the facts is **di-(9-methyl-9-fluoryl)-amine.** Thus the peculiar solubility of the salt in benzene suggests that in this solvent it is present in the dissociated form and that the base is therefore a weak one (as compared, for example, to di-(9-fluorylmethyl)-amine which would be expected to be much more strongly basic).[24] The above suggested structure for the secondary amine is in accord with the expectation that it would be formed from the amine present in largest amounts in the reaction mixture.

9-Methylphenanthridine.—9-Methyl-9-fluorylchloroamine was prepared from the hydrochloride (2.1 g.) of 9-methyl-9-fluorylamine. It was isolated as a sirup and gave a strong test for active halogen. Owing to its lability and to the difficulty in purifying it, the product in this crude form was subjected to the rearrangement conditions. When the pyridine solution of the chloramine was treated with sodium methylate a deep reddish-purple color developed and persisted until the reaction mixture was worked up. After twelve hours the pyridine was removed under diminished pressure, and the residue extracted with petroleum ether. The extract was concentrated and the material remaining dissolved in alcohol. Addition of hydrogen chloride precipitated the hydrochloride of 9-methylphenanthridine; yield 1.3 g., m. p. 287°. This was converted to the free base, which was purified by sublimation *in vacuo;* m. p. 83°. The melting point was not depressed when the material was mixed with a specimen prepared from acetyl-*o*-xenylamine.[10]

Anal. Calcd. for $C_{14}H_{11}N$: C, 87.00; H, 5.74; N, 7.28. Found: C, 86.93; H, 5.76; N, 7.13.

The picrate was prepared and crystallized from a solution of nitrobenzene and alcohol as yellow prisms; m. p. 250° (dec.).[25]

Conversion of 9-(α-Naphthyl)-9-fluorylazide to 9-(α-Naphthyl)-phenanthridine

9-(α-Naphthyl)-9-fluorylhydrazine.—Much trouble was met in attempting to prepare this type of compound. In preliminary experiments it was apparent that 9-phenyl-9-fluorylhydrazine has less favorable properties than the 9-(α-naphthyl) analog and the investigation was therefore directed toward the preparation of the latter. Owing to the unstable nature of the free base, which we were unsuccessful in preparing, the work was limited to the preparation and purification of the hydrochloride. Of the numerous experiments carried out the following directions for preparing and purifying the hydrochloride gave the best results; even in this case the salt was not quite analytically pure.

To a cooled, vigorously agitated mixture of 7 cc. of 100% hydrazine hydrate (a large excess in order to minimize the formation of the hydrazo compound) and 75 cc. of acetonitrile was gradually added, over a period of several hours, 13 g. of 9-(α-naphthyl)-9-chlorofluorene. Considerable heat was generated and after standing overnight in the ice chest the two liquid layers of the reaction mixture were separated. The solvent was removed from the upper one by distillation at room temperature under diminished pressure. The resulting residue after triturating with water was practically colorless and had an amorphous appearance; m. p. 98° with dec. and previous sintering. Conversion to the hydrochloride was effected in the manner described by Wieland[26]; yield 10 g. Repeated recrystallizations from solutions of toluene and chloroform and from solutions of alcohol and ether gave colorless prisms melting at 217° (dec.).

Anal. Calcd. for $C_{23}H_{18}N_2 \cdot HCl$: C, 76.96; H, 5.34; HCl, 10.17. Found: C, 76.02; H, 5.93; HCl (by titration), 9.43.

9-(α-Naphthyl)-9-fluorylazide was prepared in the usual manner by treating a slightly acidified aqueous alcoholic solution of the above hydrazine hydrochloride with an aqueous solution of sodium nitrite. The azide separated and was recrystallized from hexane and from 75% alcohol. It crystallized as long needles. The product was desolvated by heating in the molten state under diminished pressure; even under these conditions the process was an extremely slow one; m. p. 133°.

Anal. Calcd. for $C_{23}H_{15}N_3$: C, 82.85; H, 4.54; N, 12.65. Found: C, 82.89; H, 4.72; N, 12.23.

9-(α-Naphthyl)-phenanthridine.—The azide (0.2 g.) was decomposed by heating at 194° for ten minutes. The reaction product was extracted with boiling dilute hydrochloric acid. Upon cooling the acidic extract deposited 0.15 g. of an almost colorless hydrochloride. This was recrystallized from water and after drying at 100° melted at 224° (dec.). The free base was prepared from the hydrochloride and crystallized from hexane; m. p. 124°. The melting point of a mixture of this material with 9-(α-naphthyl)-phenanthridine prepared in a previous section was not depressed.

Summary

The Stieglitz rearrangement has been utilized

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[24] In this connection it is pertinent to call attention to solubility of 9-methyl-9-fluorylamine hydrochloride in chloroform, as compared to the insolubility of the supposed 9-fluorylmethylamine hydrochloride.

[25] Pictet and Hubert, *Ber.*, **29**, 1182 (1896), reported it to decompose at 233°.

[26] Wieland, *Ber.*, **42**, 3025 (1909).

to develop a new and practical method for the preparation of nitrogen ring compounds of the phenanthridine type. 9-Methyl-, 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine have been converted to 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-phenanthridine. That this method is not restricted to the halogenoamines is indicated by the thermal conversion of 9-(α-naphthyl)-9-fluorylazide to 9-(α-naphthyl)-phenanthridine. The primary factor in directing the course of the rearrangement of the intermediate free radical seems to be the highly strained condition of the five-membered ring in biphenylenemethylene, rather than the electronegativities of the radicals attached to the tertiary carbon atom.

WASHINGTON ,D. C. RECEIVED OCTOBER 16, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 572]

The Adjacent Charge Rule and the Structure of Methyl Azide, Methyl Nitrate, and Fluorine Nitrate

BY LINUS PAULING AND L. O. BROCKWAY

With the recognition of the fact that in many cases the normal state of a molecule cannot be represented satisfactorily by a single valence-bond structure of the Lewis type but can be approximated by a combination of several such structures (among which it is said to resonate) there arose the problem of determining for each resonating molecule the magnitudes of the contributions of various reasonable structures. Information regarding these magnitudes is being obtained in many ways, such as from the interpretation of experimental values of interatomic distances, force constants, electric dipole moments, etc., and some progress is being made in the formulation of empirical rules expressing this information in a succinct form. Four years ago it was pointed out[1] that the observed moment of inertia of nitrous oxide corresponds to resonance between the structures $:\overset{-}{\ddot{N}}=\overset{+}{N}=\ddot{O}:$ and $:N\equiv\overset{+}{N}-\overset{-}{\ddot{O}}:$, the third reasonable structure, $:\overset{=}{\ddot{N}}-\overset{+}{N}\equiv\overset{+}{O}:$, making no appreciable contribution, whereas the closely similar molecule carbon dioxide resonates among all three analogous structures; and in explanation of this unexpected fact the suggestion was advanced that, in general, structures in which adjacent atoms have electrical charges of the same sign are much less important than other structures, the diminution in importance resulting from the increase in coulomb energy corresponding to the adjacent charges. This *adjacent charge rule* was reported also to apply to the methyl azide molecule.[2] We have now reinvestigated methyl azide by electron diffraction and have similarly studied methyl nitrate and fluorine nitrate. The configurations found for all of these substances are those predicted on the basis of the rule.

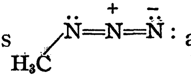
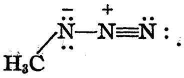
Methyl Azide.—In our earlier investigation of methyl azide[2] it was concluded that the molecules contain a linear azide group with dimensions corresponding to resonance between the structures  $H_3C-\ddot{N}=\overset{+}{N}=\overset{-}{\ddot{N}}:$ and  $H_3C-\overset{-}{\underset{..}{\ddot{N}}}-\overset{+}{N}\equiv\ddot{N}:$. The photographs used in this work were very light, showing only one measurable apparent maximum and one minimum. With improved technique we have now obtained photographs of methyl azide showing five well-defined apparent maxima, the interpretation of which has led to the verification and refinement of the earlier results. The

TABLE I

METHYL AZIDE

Max.	Min.	I	*s*, obsd.	*s*, calcd. for model H-120°	*s*, calcd. for model I-120°	C-N for model H-120°, Å.	C-N for model I-120°, Å.
1		5	6.17	6.15	6.28	1.465	1.496
2		2	8.32	8.26	8.36	1.460	1.477
	3		10.20	9.70	10.15	1.397	1.461
3		3	11.49	11.49	11.77	1.470	1.507
	4		12.75	12.47	12.70	1.437	1.464
4		1	13.81	13.68	13.66	1.455	1.454
	5		15.54	15.20	15.38	1.438	1.455
5		1	16.77	17.12	17.40	1.500	1.524
				Average C-N	=	1.453	1.480
				N-N′	=	1.246	1.229
				N′-N″	=	1.087	1.107

Averaged results:
C-N = 1.47 ± 0.02 Å.
N-N′ = 1.24 ± 0.02 Å.
N′-N″ = 1.10 ± 0.02 Å.
Angle C-N-N = 120 ± 5°

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(1) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 498 (1932).

(2) L. O. Brockway and L. Pauling, *ibid.*, **19**, 860 (1933).

sample of methyl azide used was part of that prepared for the first investigation by Dr. G. W. Wheland. The photographs were taken with a film distance of about 10 cm. and electron wave lengths of about 0.06 Å.

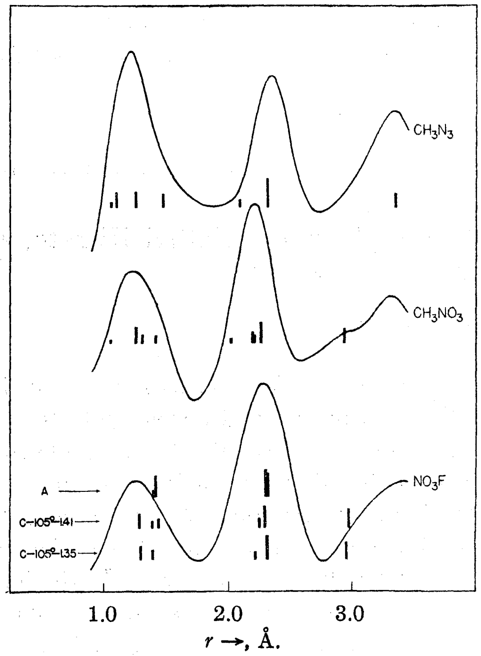
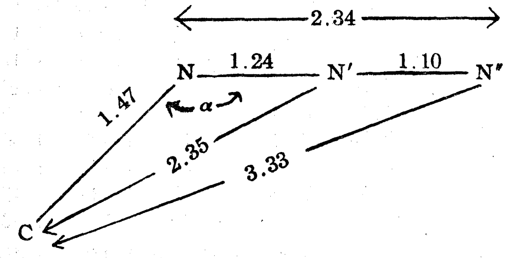


Fig. 1.—Radial distribution curves for methyl azide, methyl nitrate, and fluorine nitrate.

The measured *s* values and estimated intensities, averaged for sixteen photographs, given in Table I lead to the radial distribution curve shown in Fig. 1, with principal peaks at 1.22, 2.34, and 3.33 Å. These correspond closely with C–N = 1.47 Å. (the sum of the single-bond covalent radii), N–N = 1.24 and 1.10 Å., and the C–N–N angle = 120°, the peak at 1.22 Å. representing the unresolved distances 1.10, 1.24, and 1.47 Å. This correspondence was verified in the usual way by the comparison of the photographs with calculated intensity curves. In Fig. 2 there are shown curves for models containing a linear azide group,[3] defined by the following values of the distances N–N′ and N′–N″, respectively: E, 1.10, 1.10; F, 1.26, 1.26; G, 1.26, 1.16; H, 1.26, 1.10; I, 1.22, 1.10; the angle α having the value 180° for E and 125° for F and G, and the values shown for H and I. The C–N distance was assumed to be 1.47 Å., the C–H distances 1.06 Å., and the carbon angles were assumed to be tetrahedral. All interactions were considered, with one orientation of the methyl group.



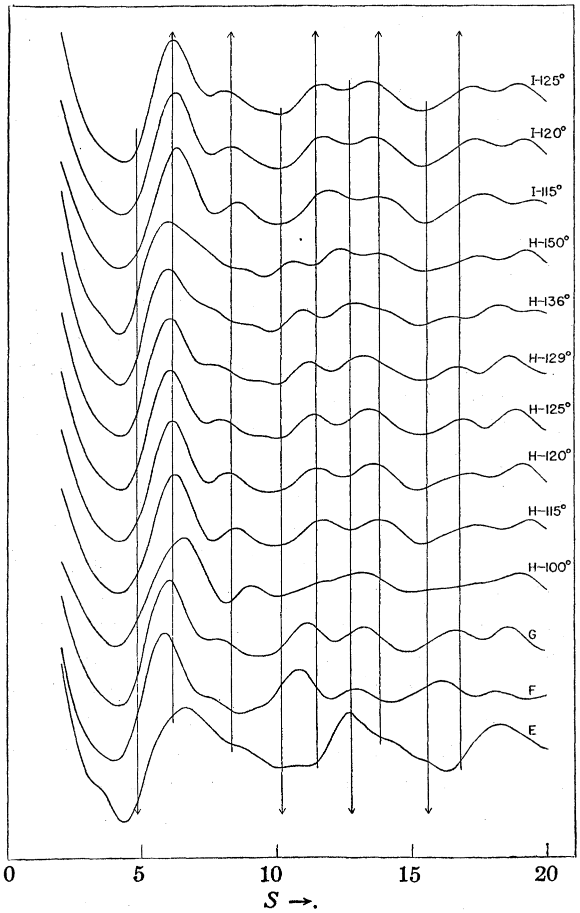


Fig. 2.—Theoretical intensity curves for methyl azide.

It is seen that all of the curves show pronounced disagreement with the photographs except H-120° and I-120° and their immediate neighbors. For these curves the qualitative and quantitative comparisons are satisfactory. The agreement for the second, third, and fourth peaks is somewhat better for the 120° curves than for the 115 or 125° curves, and we accept for the nitrogen bond angle the value 120 ± 5°, which is at the lower edge of the range of values 135 ± 15°

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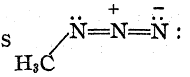
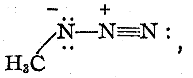
(3) The new photographs, like the old ones, are incompatible with a cyclic configuration.

previously reported. The quantitative comparison (Table I) leads to the interatomic distances C–N = 1.47 ± 0.02 Å., N–N′ = 1.24 ± 0.02 Å., and N′–N″ = 1.10 ± 0.02 Å. This final configuration of the model is identical with that indicated by the radial distribution curve.

These results are in good accord with the assumption that the molecule resonates between the two electronic structures  and , the N–N′ distance having essentially the double-bond value and the N′–N″ distance the triple-bond value.[4] The value 120° for the nitrogen bond angle, intermediate between those expected for a single and a double bond (125° 16′) and for two single bonds (109° 28′), is also not unreasonable.

Methyl Nitrate.—Methyl nitrate was prepared from methyl alcohol, nitric acid, and urea nitrate by Mr. Willard McRary under the direction of Professor H. J. Lucas. The product was washed repeatedly with water and dried, and then was redistilled three times.

The photographs show six well-defined and nearly uniformly separated rings, with *s* values and estimated intensities as given in Table II.

TABLE II

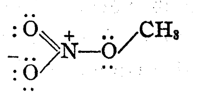
METHYL NITRATE

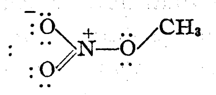
Max.	Min.	I	*s*, obsd.	*s*, calcd. for model II-105°	*s*, calcd. / *s*, obsd.
1		1	3.50	3.23	(0.923)
	2		4.67	4.17	(0.893)
2		5	6.34	6.34	1.000
	3		7.92	7.98	1.008
3		3	9.44	9.40	0.996
	4		10.69	10.50	.982
4		2	11.93	11.60	.973
	5		13.50	13.18	.976
5		1	14.87	15.20	1.022
	6		16.21	16.50	1.018
6		1	17.71	17.68	.998
				Average	0.997

Results (model II–105°): N–O = 1.26, 1.26, 1.36 Å.
O–C = 1.43 Å.
Angle N–O–C = 105 ± 5°

The six-term radial distribution function (Fig. 1) has a broad peak at about 1.24 Å., a sharper peak at 2.21 Å., and another at 3.32 Å. These are compatible with the models discussed below, but provide no basis for choice among them.

The number of parameters determining the structure of the molecule is so great that it was not possible to carry out a thorough investigation involving their independent variation. We have accordingly contented ourselves with the attempt to decide between the two most reasonable structures. The first, representing resonance among the three structures A, B, and C, leads to the predicted dimensions shown below, all three N–O bonds having approximately the double bond distance. The methyl group is restricted to the plane of the nitrate group by the double-bond character of the N–OCH$_3$ bond. For α a value of about 120 or 125° would be expected; curves calculated for 120, 125, and 130° are shown in Fig. 3. The second reasonable structure, representing resonance between A and B only, corresponds to essentially the double-bond distance for two of the N–O bonds and the single-bond distance for the third. Steric effects probably tend to keep the methyl group out of the plane of the nitrate group. The curves of Fig. 3 are calculated on this assumption; we have found that they are changed only slightly by the assumption of free rotation of the OCH$_3$ group about the N–O bond. For α a value close to the tetrahedral value 109° 28′ is expected; curves for α = 100, 105, 110, and 115° are shown.


A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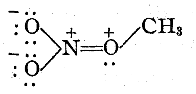
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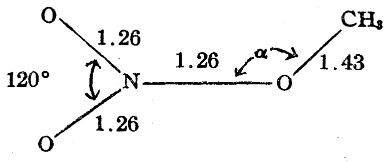

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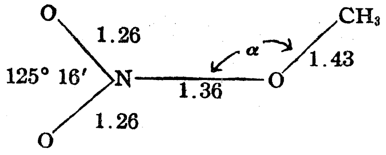

II

All of the curves show rough agreement with the photographs; the curves for model I are,

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[4] L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

however, all inferior to curve II–105° in regard to the observation of six well-shaped and nearly uniformly spaced rings. Curve II–105° is in nearly complete agreement with the experimental data, the greatest quantitative discrepancy, 3%, being shown by the fourth maximum (see Table II). We accordingly accept model II with α = 105° as supported by the electron diffraction data. The quantitative comparison verifies the interatomic distance values N–O = 1.36 Å. (for the oxygen atom with methyl attached), N–O = 1.26 Å. (for the other oxygen atoms), and O–C = 1.43 Å. to about ± 0.05 Å., the N–O–C bond angle being given the value 105 ± 5°. This configuration is compatible with the radial distribution curve (Fig. 1).

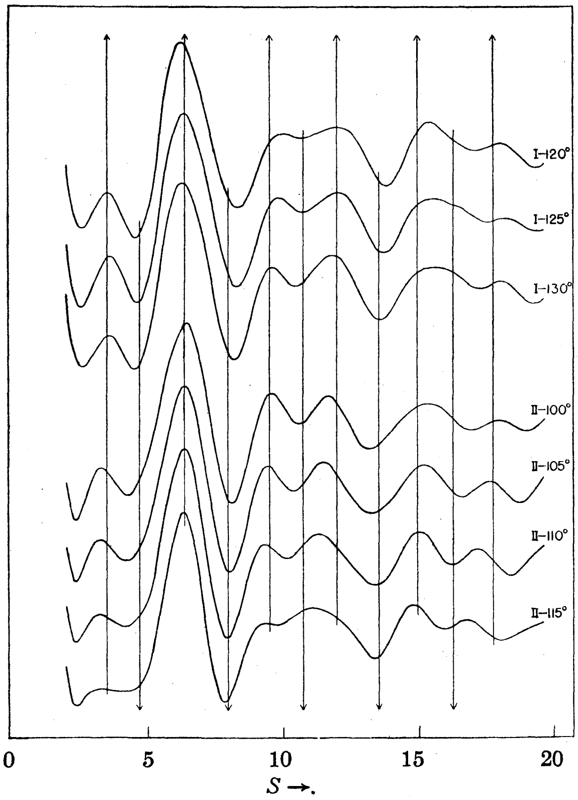

Fig. 3.—Intensity curves for methyl nitrate.

Fluorine Nitrate.—Fluorine nitrate, NO_3F, was first prepared by G. H. Cady[5] in 1934 by bubbling fluorine through dilute nitric acid. At the suggestion of Professor W. A. Noyes, we undertook the electron diffraction investigation of the vapor in order to determine where the fluorine atom is attached and what effect it has on the nature of the bonds in the NO_3 group. Professor D. M. Yost and Mr. A. Beerbower of these Laboratories[6] prepared samples of fluorine nitrate by Cady's method (using the original apparatus of Dr. Cady), and also by another method, consisting in passing fluorine over solid potassium nitrate, and kindly provided us with some of the substance for the electron diffraction work. The vapor of the substance at about 300 mm. pressure was held in a one-liter glass flask connected to the electron diffraction apparatus through an ordinary stopcock. The photographs obtained from the first sample showed four rings. An attempt to prepare heavier photographs from another sample was made unsuccessful by the explosion of the substance at the instant of making the first exposure. It was previously thought that fluorine nitrate gas was stable at room temperature, and the cause of the explosion is still unknown.

The s values and the visually estimated intensities for the four rings observed in the photographs are given in Table IV. The radial distribution function (Fig. 1) shows maxima at 1.27 and 2.29 Å., the second being about twice as large as the first.

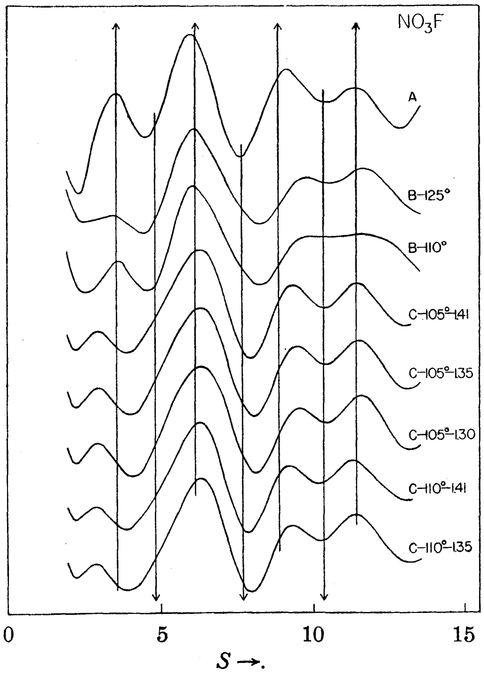

Fig. 4.—Intensity curves for fluorine nitrate.

The molecular models upon which the theoretical intensity curves of Fig. 4 are based have been chosen to distinguish between the three most probable configurations of fluorine nitrate. The

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[5] G. H. Cady, THIS JOURNAL, **56**, 2635 (1934).

[6] D. M. Yost and A. Beerbower, *ibid.*, **57**, 781 (1935).

first, suggested to us by Professor W. A. Noyes, involves a tetrahedral arrangement of the fluorine and oxygen atoms around the nitrogen atom, in which the bond angles are all 109° 28′ and the ratio of the N–F to the N–O distances is 0.985; the corresponding curve is marked A. The other two models are similar to those considered above for methyl nitrate. In the second (B) the double bond in the NO_3 groups is assumed to resonate equally among the three N–O bonds and the fluorine atom lies in the plane of the other atoms, with the interatomic distances as shown in Table III. In the third (C) the resonance of the double bond does not involve the oxygen atom to which the fluorine is attached (O′) but is restricted to the other two positions; with this structure the molecule is no longer coplanar but instead the NO′F plane is perpendicular to the NO_3 plane.

TABLE III

MODELS FOR NO_3F

Model	NO	NF	NO′	O′F	<ONO	<NO′F
A	1.40	1.38			109° 28′	
B–125°	1.26		1.26	1.34	120°	125°
B–110°	1.26		1.26	1.34	120°	110°
C–105°–1.41	1.26		1.36	1.41	125°	105°
C–105°–1.35	1.26		1.36	1.35	125°	105°
C–105°–1.30	1.26		1.36	1.30	125°	105°
C–110°–1.41	1.26		1.36	1.41	125°	110°
C–110°–1.35	1.26		1.36	1.35	125°	110°

The models for complete resonance, B, are eliminated because in the corresponding curves the third and fourth maxima are not well resolved from each other, as they are in the photographs. The remaining six curves are more satisfactory in this respect, the relative heights of the third and fourth maxima showing better agreement with the photographs for the curves A, C–105°–1.41, and C–105°–1.35 than for the other three.

TABLE IV

FLUORINE NITRATE

Max.	Min.	I	s, obsd.	s, calcd. C–105° –1.41	s, calcd. C–105° –1.35	s, calcd./s, obsd. C–105°–1.41	s, calcd./s, obsd. C–105°–1.35
1		2	3.56	2.95	2.97	(0.829)	(0.834)
	2		4.84	3.87	3.97	(0.800)	(0.821)
2		5	6.16	6.29	6.29	1.021	1.021
	3		7.66	7.89	8.04	1.030	1.050
3		2	8.88	9.34	9.46	1.052	1.065
	4		10.36	10.36	10.41	1.000	1.005
4		1	11.45	11.46	11.52	1.001	1.006
					Average	1.021	1.029
					N–O	1.286 Å.	1.296 Å.
					N–O′	1.389	1.400
					O–F	1.440	1.390

Model A cannot be eliminated definitely by the photographs; there are, however, some points which make this model improbable. From the curve for this model the first minimum would be expected to be at least as well pronounced as the second minimum, whereas on the photographs the first minimum is not very well defined. That the qualitative appearance of the photographs supports model C rather than model A is further shown by the fact that the photographs resemble those of methyl nitrate more closely than those of carbon tetrafluoride. Some evidence is also provided by the radial distribution curve (Fig. 1), the first peak being displaced by 0.15 Å. from the position expected for it for model A. For these reasons and the additional reason that it is difficult to correlate the tetrahedral configuration with an electronic structure involving only completed octets, we consider model A not to be satisfactory.[7]

The curves C–105°–1.41 and C–105°–1.35 are in reasonably good qualitative and quantitative agreement with the photographs, the discrepancies shown by the first maximum and second minimum being no larger than usual for inner rings. The quantitative comparison (Table IV) leads to the average interatomic distances N–O = 1.29 Å., N–O′ (with fluorine attached) = 1.39 Å., and O′–F = 1.42 Å., with probable errors of about ± 0.05 Å. The bond angles are O–N–O = 125 ± 5° and N–O′–F = 105 ± 5°. This configuration is compatible with the radial distribution curve (Fig. 1).

The Adjacent Charge Rule.—There are thus now known four substances (nitrous oxide, methyl azide, methyl nitrate, and fluorine nitrate) with configurations supporting the adjacent charge rule. That this rule is reasonable can be seen from the following argument. In general a valence-bond structure involving two charged atoms with opposite signs may correspond to about the same energy value as a structure involving uncharged atoms, the difference between the ionization energy of one atom and the electron affinity of the other being approximately compensated by the coulomb energy of the charges. For example, the coulomb interaction of the charges + *e* and − *e* 2.30 Å. apart stabilizes the structures $:\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}{-}C{\equiv}O\overset{+}{:}$ and $:\overset{+}{O}{\equiv}C{-}\underset{\cdot\cdot}{\ddot{O}}\overset{-}{:}$ for carbon dioxide by 6.3 e. v., which

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[7] Quantitative comparison for this model leads to the interatomic distances N–O = 1.42 Å., N–F = 1.40 Å.

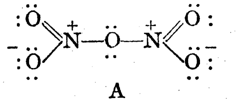
is roughly equal to the estimated energy required to remove an electron from one bound oxygen atom and attach it to another; it is accordingly not unreasonable that these two structures contribute about equally with the structure $:\ddot{O}=C=\ddot{O}:$ to the normal state of the molecule. For nitrous oxide the two structures $\bar{:}\ddot{N}=\overset{+}{N}=\ddot{O}:$ and $:N\equiv\overset{+}{N}-\ddot{O}\bar{:}$ have nearly equal covalent bond energies and coulomb energies and would be expected to make about equal contributions. The structure $\bar{:}\ddot{N}-\overset{+}{\underset{\cdot\cdot}{N}}\equiv\overset{+}{O}:$, however, with adjacent positive charges adding a large positive quantity to the energy of the molecule, corresponds to a higher energy value than the other two structures, and accordingly makes no significant contribution to the normal state of the molecule.

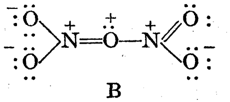
The principal application of the adjacent charge rule is to the compounds of nitrogen. In many compounds a nitrogen atom forms four covalent bonds and has a positive charge; the adjacent charge rule then prevents resonance to structures in which an atom attached to this nitrogen atom also has a positive charge. The covalent azides and nitrates are the principal substances of this type. It is interesting to note that the adjacent charge rule provides an explanation of the large differences in stability shown by covalent and ionic azides and nitrates. Covalent azides and nitrates are restricted by the rule to resonance between two important structures, whereas the ions resonate among three structures. The resonance energy[8] for two structures is about 1 e. v. and for three structures about 2 e. v.; hence ionic azides and nitrates are more stable than the covalent substances by about 25,000 cal. per mole. We accordingly understand why the alkali and alkaline earth azides[9] can be exploded only at high temperatures whereas the heavy metal azides, chlorazide, cyanuric triazide, and other covalent azides are extremely explosive. Similarly the ionic nitrates are relatively stable, whereas the covalent nitrates (methyl nitrate, nitroglycerine, etc.) are exploded easily. It may be pointed out that the covalent nitrates are more closely related to nitro compounds than to the nitrate ion from the resonance point of view, in that in covalent nitrates, as in nitro compounds, the double bond resonates between two oxygen molecules, whereas in the nitrate ion it resonates among three.

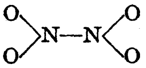
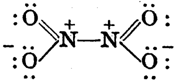
The destabilizing effect of the adjacent charge rule shown in covalent nitrates does not occur in the analogous compounds containing carbon as the central atom, such as carbonates, urea, guanidine, etc., since the quadricovalent carbon atom is neutral.

The question as to whether or not hydrazoic acid and nitric acid are more closely related to the corresponding covalent compounds than to the ions could be answered by determining the configurations of the acids. From general information we would predict that the H–N and H–O bonds are essentially covalent (with perhaps about one-third ionic character) and that the N_3 and NO_3 groups in the acids have the same structures as in methyl azide and nitrates. This prediction is supported by the instability of the acids.

The adjacent charge rule permits resonance of nitrogen pentoxide among the four structures of type A, but excludes the four structures of type B (as well as the structure with two double bonds to the central oxygen atom). We accordingly predict for the molecule a configuration in which the two interatomic distances N–O′ (O′ being the central oxygen atom) have about the single-bond value 1.36 Å. and the four distances N–O have about the double-bond value 1.26 Å., each NO_3 group being coplanar, with the angles ONO equal to about 125° and NO′N to about 110°; the relative orientation of the two NO_3 planes is uncertain, since the single N–O′ bonds permit free rotation.[10]


A


B

The symmetrical configuration  is usually assumed for nitrogen tetroxide.[11] However, the only reasonable electronic structures involving completed octets which can be written for this configuration are the four of the type  which are incompatible with

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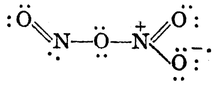
[8] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

[9] The alkali azides are known to be ionic: S. B. Hendricks and L. Pauling, THIS JOURNAL, **47**, 2904 (1925); L. K. Frevel, *ibid.*, **58**, 779 (1936).

[10] L. R. Maxwell, V. M. Mosley and L. S. Deming, *J. Chem. Phys.*, **2**, 331 (1934), report the values N–O = 1.18 Å. and N–O′ = 1.3–1.4 Å. on the basis of electron diffraction data, in agreement with our structure.

[11] S. B. Hendricks, *Z. Physik*, **70**, 699 (1931); G. B. B. M. Sutherland, *Proc. Roy. Soc.* (London), **A141**, 342, 535 (1933); Maxwell, Mosley and Deming, ref. 10; L. Harris and G. W. King, *J. Chem. Phys.*, **2**, 51 (1934).

the adjacent charge rule. We accordingly believe that nitrogen tetroxide has not this configuration but instead the unsymmetrical configuration corresponding to resonance between the two structures of type .

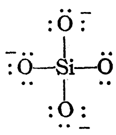
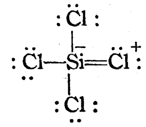
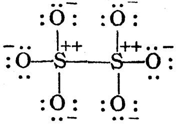
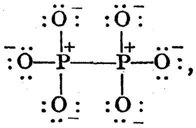
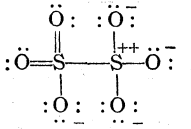
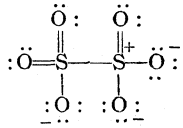
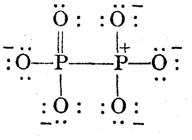
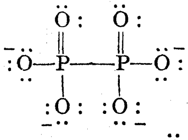
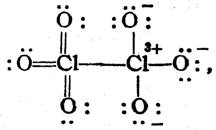
The adjacent charge rule provides some information regarding the nature of the bonds in the oxygen acids of heavier atoms. It has become customary, following Lewis, to assign to the silicate ion and related groups structures such as , the octet rule being considered to hold for the heavier atoms as well as for the first-row atoms. The discovery of Brockway and Wall[12] that structures such as  are important for silicon tetrachloride and other halides of non-first-row atoms suggests that corresponding structures might be important for the oxygen compounds also. Strong support for this idea is provided by the observed interatomic distances in crystals, as determined by W. L. Bragg, Zachariasen, and others, which are approximately equal to the sums of double-bond radii (Table V), indicating strong resonance to structures involving double bonds.[13] Dithionic acid, $H_2S_2O_6$, and hypophosphoric acid, $H_4P_2O_6$, are stable substances, resisting oxidation even by dichromate.[14] This stability would not be expected for the completed octet structures  and , which run counter to the adjacent charge rule; the rule instead requires us to accept as the important structures for these substances those in which a sulfur atom forms two double bonds and a phosphorus atom one double bond, such as ,  etc., and ,  etc.

TABLE V

INTERATOMIC DISTANCES M–O IN IONS MO_4

	SiO_4^{4-}, Å.	PO_4^{3-}, Å.	$SO_4^{=}$ Å.	ClO_4^{-}, Å.
Observed values	1.60	1.53	1.50	1.48
Sums of single-bond radii	1.83	1.76	1.70	1.65
Sums of double-bond radii	1.65	1.58	1.53	1.48

For Cl_2O_6 structures such as , etc., are allowed by the adjacent charge rule. We consider it probable that the dissociation of this substance is due not to its instability (weakness of the Cl–Cl bond) but instead to the unusual stability of the odd molecule ClO_3 through three-electron bond formation, as in the other odd molecules NO_2, NO, ClO_2, etc. It is possible that Cl_2O_6 has an unsymmetrical configuration, $O_3Cl–O–ClO_2$, analogous to that which we have suggested for N_2O_4; however, chlorine, unlike nitrogen, has more than four orbitals in its outer shell and hence the adjacent charge rule does not eliminate the symmetrical configuration, which we consider to be the more likely one because of analogy with the dithionate and hypophosphate ions.

We wish to thank Dr. G. H. Cady for lending us his apparatus, Professor Don M. Yost and Mr. A. Beerbower for preparing the fluorine nitrate used in this work, Mr. K. S. Palmer for assisting in the preparation of the electron diffraction photographs, and Dr. Sidney Weinbaum and Mrs. M. Lassettre for assisting in their interpretation.

Summary

The investigation of methyl azide, methyl nitrate, and fluorine nitrate by electron diffraction is shown to lead to configurations of the molecules corresponding in each case to resonance between two important valence-bond structures. The unimportance of a third otherwise reasonable structure for these molecules as well as for nitrous oxide is ascribed to instability due to the presence of electric charges of the same sign on adjacent atoms. It is shown that the differ-

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[12] L. O. Brockway and F. T. Wall, THIS JOURNAL, 56, 2373 (1934).

[13] The observed decrease below the double-bond values may possibly be due to some triple bond formation.

[14] P. Nylén and O. Stelling, *Z. anorg. allgem. Chem.*, 212, 169 (1933).

ences in chemical properties of covalent and ionic azides and nitrates can be correlated with differences in structure. The use of the adjacent charge rule is illustrated by its application in the discussion of the structures of nitrogen pentoxide, nitrogen tetroxide, and the oxygen acids of heavier atoms.

PASADENA, CALIF. RECEIVED OCTOBER 19, 1936

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Reaction between Osmium Tetroxide and Hydrobromic Acid. II. Rate Study

BY H. DARWIN KIRSCHMAN AND WILLIAM R. CROWELL[1]

In a previous article on a study of the equilibrium between osmium tetroxide, hydrogen ion and bromide ion at 100°, it was suggested that at low acid and high bromine concentrations the reaction might be of the type[2]

$$OsO_4 + H^+ + {}^5/_2Br^- \rightleftharpoons Os(OH)O_3^-Br + {}^1/_2Br_3^- \quad (1)$$

The purpose of the present work was to carry out a study of the rate of the reaction between osmium tetroxide, hydrogen ion and bromide ion with a view of learning more of its nature and to determine, if possible, the validity of certain assumptions made in the earlier investigation.

The general plan of the work consisted of the analysis for bromine of the contents of the reaction tubes at various time intervals in experiments conducted in a manner similar to that employed in the equilibrium problem. From the results obtained an attempt was made to determine the order of the reaction with respect to octavalent osmium, hydrogen ion and bromide ion.

The general form of the rate expression can be stated as

$$-\frac{d(OsO_4)}{dt} = k(Os_8)^a\ (H^+)^b\ (Br^-)^c\ \frac{(f_1)^a\ (f_2)^b\ (f_3)^c}{f_4}$$

In the present instance $k = k_0K$ where k_0 is the specific reaction rate constant and K the equilibrium constant of the intermediate complex. f_1, f_2, f_3 and f_4 are the activity coefficients of octavalent osmium, hydrogen ion, bromide ion and the intermediate complex, respectively.

In the first series of experiments, the initial concentration of all the reacting constituents was kept constant except that of the osmium, which was changed about twofold. A second series of runs was made at different concentrations of hydrobromic acid but at a fixed initial concentration of osmium. A third series of runs was made at approximately constant ionic strength and at the same initial concentration of octavalent osmium. Some of these runs were carried out at different concentrations of bromide ion but at a fixed concentration of hydrogen ion. In other runs the bromide ion concentration remained constant while the hydrogen ion concentration was changed. The purpose of the experiments at constant ionic strength was to determine the orders with respect to hydrogen and bromide ion, and to see if the sum of these orders was approximately equal to the order with respect to hydrobromic acid found in the second series of runs. Finally, using the rate data thus obtained, a series of rate constants was calculated.

Experimental

The apparatus was that employed in the equilibrium experiments.[2] The potassium hydroxide solution of osmium tetroxide was prepared as described in our previous article on the determination of octavalent osmium.[3] The hydrobromic acid was prepared from red phosphorus and bromine by the well known method. The middle fraction of the distillate was redistilled until a water white product was obtained.

The experimental procedure was essentially the same as that used in the equilibrium experiments with one modification in the case of the solutions 1.2 and 1.6 *M* in hydrobromic acid. In these solutions there was a tendency for the bromine formed to react with the reduced osmium when the tubes were broken in the chilled water in the titration beaker. To overcome this difficulty, sufficient hydrobromic acid was added to the water in the titration beaker to make the acid concentration after the addition of the contents of the reaction tube about 0.1 *N*.

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(1) The authors were assisted in the experimental work by Messrs. Glen Seaborg and Robert Brinton, students in the Chemistry Department at the University of California at Los Angeles.

(2) Kirschman and Crowell, THIS JOURNAL, **55**, 488 (1933).

(3) Crowell and Kirschman, *ibid.*, **51**, 175 (1929).

TABLE I

CONCENTRATION OF REDUCED OSMIUM AT VARIOUS TIME INTERVALS AT 100°

In moles per 1000 grams of water × 10^3

	Concn. in moles per 1000 g. of water				Reaction time in hours										
Runs	$OsO_4 \times 10^3$	HBr	KBr	KCl	1/24	1/12	1/6	1/4	1/3	1/2	1	2	4	8	24
1	4.30	1.24	..	..	..	...	...	0.210	..	0.355	0.670	1.05	1.61	2.04	2.31
2	4.28	1.66	..	..	..	...	...	.479	..	1.12	1.92	2.28	2.48	2.59	2.61
3	4.36	2.10	..	..	..	...	0.840	...	1.68	2.24	2.66	2.70	2.62	2.72	
4	4.34	2.55	..	..	..	0.806	1.88	2.67	3.08	3.31	3.38				
5	2.04	2.55	..	..	..	.408	0.816	1.10	..	1.59	1.69	1.69			
6	4.48	3.50	..	..	1.76	3.54	4.32	4.32							
7	2.07	3.50	..	..	0.880	1.80	2.01	2.01							
					Runs at Approximately Constant Ionic Strength										
8	4.15	1.31	..	2.18	..	...	...	0.95	..	1.90	2.64	2.90	2.90		
9	4.15	1.31	1.31	0.88	0.33	0.91	1.84	2.34	..	2.84	3.06				
10	4.15	1.31	2.18	..	.43	.93	2.04	2.68	..	3.01					
11	4.15	1.75	..	1.75	..	.66	...	1.88	..	2.79	2.93	3.06	3.18		
12	4.15	1.75	1.75	..	..	1.39	2.80	3.22	..	3.35	3.37				
13	4.15	2.62	..	0.88	.85	1.96	3.53	3.83							
14	4.15	2.62	0.88	..	..	2.54	4.00	4.00							

Results of the Rate Experiments

Table I shows results of rate experiments at 100°. All concentrations of reduced osmium are expressed in moles per 1000 g. of water. Runs 1–7 inclusive are at different concentrations of octavalent osmium and of hydrobromic acid, while runs 8–14 inclusive are at the same osmium concentration and approximately at the same ionic strength as the hydrobromic acid run at 3.50 *M*. In order to keep the solutions at the same ionic strength for different concentrations of hydrogen ion and bromide ion, potassium bromide and potassium chloride were used in addition to the hydrobromic acid. While these salts, particularly potassium chloride, may influence the nature of the reduced osmium complexes, they should not affect markedly the initial rates.

The initial rates were obtained by plotting the data in Table I and obtaining the slopes of the curves by well-known graphical methods. The values for the individual runs are shown in column 2 of Table II. The order of the reaction n_r with respect to any reactant was calculated from the expression

$$n_r = \frac{\text{Log rate ratio}}{\text{Log activity ratio}}$$

By comparing run 4 with run 5, and run 6 with run 7, the effect of doubling the osmium concentration in a fixed concentration of hydrobromic acid was determined. The average of the two values of n_{OsO_4} was 0.98.

In runs 1, 2, 3, 4 and 6 the concentration of osmium was approximately the same while the concentration of acid was changed in steps from 1.24 to 3.50 *M*. The runs compared were 1 and 2, 1 and 3, 1 and 4, 1 and 6, 2 and 3, 2 and 4, and 2 and 6, 3 and 4, 3 and 6, and 4 and 6. To calculate the activity of the hydrobromic acid, the activity coefficients shown in Table II column 5 were used. It was assumed that the ratio of the activity coefficients of the octavalent osmium and the intermediate complex was constant. The calculated order with respect to hydrobromic acid varied from 2.5 to 1.9. For the most part the higher values were obtained when comparing the lower acid concentrations. The average of the series of ten values was 2.17.

TABLE II

INITIAL RATES AND RATE CONSTANTS

Runs	Ionic strength moles per 1000 g. H_2O	$-(OsO_4)/dt$ moles per 1000 g. H_2O per hr. × 10^3	Specific rate $k' \times 10$	$\gamma \pm$ at 100°	Rate constant $k \times 10$
1	1.24	0.84	1.30	0.88	1.7
2	1.66	2.14	1.80	.99	1.8
3	2.10	5.04	2.66	1.14	2.0
4	2.55	10.9	3.87	1.33	2.2
5	2.55	4.92	3.72	1.33	2.1
6	3.50	43.2	7.86	1.94	2.1
7	3.50	21.6	8.55	1.94	2.3
8	3.50	3.79	5.46	1.26	3.4
9	3.50	10.9	7.52	1.26	4.7
10	3.50	12.2	6.50	1.26	4.1
11	3.50	8.2	6.50	1.37	3.5
12	3.50	16.8	6.50	1.37	3.5
13	3.50	23.4	8.20	1.63	3.1
14	3.50	30.4	7.90	1.63	3.0

In runs 8 to 14, inclusive, in which the ionic strength was kept constant, the order with respect to bromide ion was calculated by comparing runs 8 and 9, 8 and 10, 11 and 12 and 13 and 14. While it is realized that the activity coefficient of hydrobromic acid in the solutions used is not exactly constant at constant ionic strength, this fact does not prevent fair estimates of the order being made. The average value of n_{Br^-} was 1.18. The order with respect to hydrogen ion was obtained by comparing runs 6 and 10, 6 and 12, 9 and 13 and 10 and 14. In this case the average value of n_{H^+} was 1.22. Although the general tendency is for the orders in both series to run somewhat above unity, this is presumably due to the fact that the activity effects are not the same in all of the solutions. It seems reasonable to suppose that the order with respect to both bromide and hydrogen ion is one, and this checks fairly well with the results obtained with hydrobromic acid solutions containing no salt. These results indicate that the assumption that the intermediate complex is neutral in character is justified.

In the light of the results described, the rate expression can take the form

$$-\frac{d(OsO_4)}{dt} = k(Os_8)(H^+)(Br^-)(\gamma\pm)^2$$

whence

$$k = -\frac{d(OsO_4)}{dt} \times \frac{1}{(Os_8)(H^+)(Br^-)(\gamma\pm)^2} = \frac{k'}{(\gamma\pm)^2}$$

where $\gamma\pm$ represents the mean ion activity coefficient of the hydrobromic acid.

Table II shows results of calculations of k' and k made in accordance with the above expressions. The activity coefficients were calculated from recent data of Harned[4] obtained from measurements made on solutions of hydrobromic acid and mixtures of hydrobromic acid and potassium bromide. In this calculation it was necessary to make a small extrapolation from 3.0 to 3.5 *M*, and also to correct the values to 100° by use of thermal data given in the "International Critical Tables."[5,6]

Attention is called to the fact that the constants for experiments 1–7 inclusive are in very fair agreement and the same is true for experiments 8–14 inclusive. The value of k for the latter group is definitely higher than that for the former group. The reason for this is not evident, but may be due to uncertainties in the values of γ_{HBr} in these solutions. It is a curious fact that the assumption that γ_{HBr} is equal for all solutions of ionic strength 3.5 *M* leads to better constancy of k for experiments 8–14 as well as to a much better agreement between the k's of both series of experiments.

Conclusions

Since the results indicate that the reaction in the rate determining step is first order with respect to octavalent osmium, hydrogen ion and bromide ion, the mechanism that is suggested for the initial stages of the reaction is as follows.

$$H_2OsO_5 + H^+ + Br^- \longrightarrow H_2OsO_4 + HBrO \qquad (2)$$
(Rate determining step)

$$HBrO + H^+ + Br^- \longrightarrow Br_2 + H_2O \qquad (3)$$
(Rapid follow reaction)

$$Br_2 + Br^- \longrightarrow Br_3^- \qquad (4)$$
(Rapid follow reaction)

$$H_2OsO_4 + {}^1/_2Br_3^- \longrightarrow HOsO_4 + H^+ + {}^3/_2Br^- \qquad (5)$$
(Rapid follow reaction)

$$HOsO_4 + Br^- \longrightarrow Os[(OH)O_3Br]^- \qquad (6)$$
(Rapid follow reaction)

The sum is (1).

The formation of hexavalent and heptavalent forms other than those shown is, of course, quite possible.

In the previous work on the equilibrium study the statement was made that the equilibrium constants indicated that the tendency was for the octavalent osmium to be reduced to the heptavalent state in solutions of low acid and high bromine concentration and that at high acid and low bromine concentration the tendency was toward reduction to the quadrivalent state. The present work seems to show that in all the solutions, 1.2 *M* as well as 3.5 *M* in hydrobromic acid with or without potassium bromide or chloride, the first step of the reaction is a reduction of OsO_4 to the hexavalent state. In solutions of low acid concentration the hexavalent osmium is oxidized to the heptavalent form by rapid follow reactions. With increasing acid concentration some of the rapid follow reactions lead more and more to a reduction to the quadrivalent form with the setting up of more or less complicated equilibria. In all the solutions in which the bromine is not confined in the reaction tubes, the net effect is a reduction to the quadrivalent form.

In conclusion we wish to express our appreciation to Dr. Don M. Yost for his valuable assistance in this work.

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[4] Harned, This Journal, 57, 1865 (1935).

[5] "International Critical Tables," Vol. V, p. 177.

[6] It should be noted that in the equilibrium study described in a former paper[2] the application of these new values of $\gamma\pm$ will change the absolute values of the equilibrium constant quite radically. The relative values, however, will still be in sufficient accord to justify the conclusions then drawn.

Summary

The rate of the reaction between osmium tetroxide, hydrogen ion and bromide ion at 100° in acid concentrations from 1.2 to 3.5 M has been studied and the reaction in the rate determining step has been found to be of the first order with respect to each of the reacting constituents.

On the basis of this study and an earlier investigation of the equilibrium between octavalent osmium, hydrogen ion, bromide ion, reduced osmium and tribromide ion a mechanism has been suggested indicating the steps in the initial stages of the reaction. In all the acid solutions the first and rate determining step is a reduction of the osmium to the hexavalent state. In solutions of low acid and high bromine concentration, rapid follow reactions carry the osmium to the heptavalent state, but in solution of high acid and low bromine concentration the tendency is toward the quadrivalent form.

In the expression

$$k = -\frac{d(OsO_4)}{dt} \times \frac{1}{(Os_8)(H^+)(Br^-)(\gamma\pm)^2}$$

the value of k has been found to be approximately 0.28 when the time is expressed in hours.

LOS ANGELES, CALIF. RECEIVED OCTOBER 19, 1936

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

Electrochemical Properties of Diphenylbenzidine Sulfonic Acid

BY L. A. SARVER AND I. M. KOLTHOFF

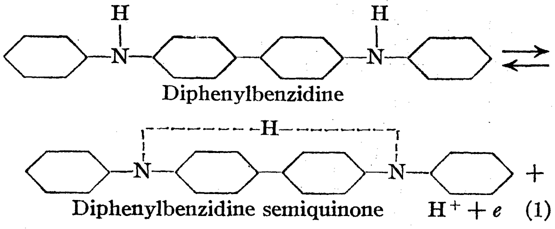
It has been mentioned in previous work[1] that upon oxidation of a substituted aromatic diamine such as diphenylbenzidine there is first formed a green insoluble intermediate product, and then a more soluble violet quinoid compound of high coloring power.

The intermediate product was assumed to be a meriquinone, or double molecular compound composed of one molecule of the diphenylbenzidine itself and one molecule of the oxidized quinoid form; but no proof has ever been presented as to the correctness of this view, and from the recent work of Michaelis[2] it was thought possible that the green substance might be a semiquinone, or compound derived from diphenylbenzidine by the transfer of one electron instead of two.

It has been proved in a number of cases by electrochemical means that the intermediate oxidation products of diamines are really semiquinones and not meriquinones, but this has never been achieved for a compound of the benzidine series because of the insolubility and instability of the oxidation products. The green product from diphenylbenzidine itself is extremely insoluble, while that from diphenylbenzidine disulfonic acid is only slightly soluble. However, a polysulfonic acid of diphenylbenzidine has been obtained recently[3] which gives a fairly soluble and stable green oxidation product, and it appeared that with this substance it might be possible to decide whether or not semiquinones are formed by compounds of the benzidine series.

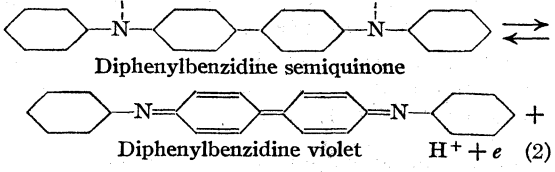
Since the only function of the sulfonic acid groups is to increase the solubility of the reagent and its oxidation products, let us consider the mechanism for the oxidation of diphenylbenzidine itself. We shall call the first and second oxidation products diphenylbenzidine green and diphenylbenzidine violet, respectively.

According to the semiquinone theory, the first stage of the oxidation should be:


Diphenylbenzidine

Diphenylbenzidine semiquinone H$^+$ + e (1)

where e represents an electron transferred; the second stage would then be


Diphenylbenzidine semiquinone

Diphenylbenzidine violet H$^+$ + e (2)

According to the meriquinone theory, on the other hand the first stage of the reaction would be

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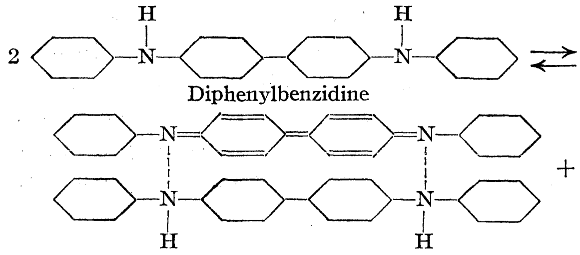
[1] I. M. Kolthoff and L. A. Sarver, THIS JOURNAL, **52**, 4179 (1930).

[2] See L. Michaelis, *Chem. Rev.*, **16**, 243 (1935), where references to earlier work may be found.

[3] L. A. Sarver and Wm. Von Fischer, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 271 (1935).



Diphenylbenzidine meriquinone $2H^+ + 2e$ (3)

and the second stage would be

$$\text{Diphenylbenzidine meriquinone} \rightleftarrows 2 \text{ diphenylbenzidine violet} + 2H^+ + 2e \quad (4)$$

If the number of moles of diphenylbenzidine taken for titration is represented by a, and the number of moles oxidized at any time by x, the potentials during the first stage of the reaction should be given by

$$E = E_0 + \frac{RT}{F} \log \frac{x}{a - x}, \text{ at constant } p\text{H} \quad (5)$$

if the green compound is a semiquinone, and by

$$E = E_0 + \frac{RT}{2F} \log \frac{[\text{M. Q.}]}{[\text{D. B.}]^2}, \text{ at constant } p\text{H} \quad (6)$$

if it is meriquinone.

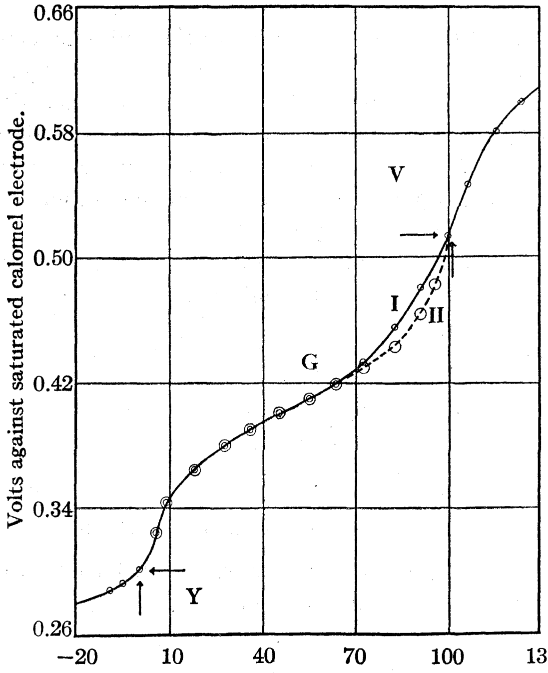


Fig. 1.—I, potentials observed; II, potentials calculated as semiquinone; $E = 0.405 + 0.06 \log([\text{D. B. semiquinone}]/[\text{D. B.}])$; V, violet; G, green; Y, yellow.

Similar equations apply to the second stage of the reaction.

By a comparison of the shapes of the experimental titration curves with those calculated on the basis of the formation of semiquinones and meriquinones, respectively, it should be possible to decide which theory is correct in this case.

Experimental

The diphenylbenzidine sulfonic acid used was prepared and purified by the method of Sarver and von Fischer,[3] and a microscopical examination revealed no appreciable amount of sodium sulfate to be present. Upon ignition, an amount of sodium sulfate corresponding to 52.7% of the sample was obtained; a compound with ten sulfonic acid groups should give 52.1%. Stock solutions in water were prepared which contained 1 g. of the yellow sodium salt per liter, and suitable quantities of sulfuric acid were added in each experiment just before titration.

The reduction potential of ferrous iron in sulfuric acid solution was not sufficiently low to effect complete reduction of the green compound, but in the presence of fluoride the change from green to yellow, indicating complete reduction of the green, occurred at approximately 0.30 v., against the saturated calomel electrode (or at 0.55 v., against the normal hydrogen electrode), in 1.0 N sulfuric acid solution.

Attempts were made to titrate portions of the diphenylbenzidine sulfonic acid with bromine in a buffered solution at a pH of 4, but the oxidation products decomposed so rapidly that no steady potentials could be obtained. However, when the titrations were performed in 1.0 N sulfuric acid, using standard solutions of potassium dichromate and ferrous iron in the same concentrations of sulfuric acid, potentials were obtained which were subject to very little drift, at least during the first stage of the oxidation. The best results were obtained by adding a slight excess of dichromate over that theoretically required for the oxidation of all the diphenylbenzidine sulfonic acid to the corresponding green, allowing the system to come to equilibrium, then adding some hydrofluoric acid to lower the potential of the ferrous–ferric iron system, and back-titrating with standard ferrous solution.

In this way, some very good titration curves were obtained (Fig. 1), which showed distinct breaks at the disappearance of the violet and green, respectively. In a large number of experiments, 1.7 ml. of 0.01 N dichromate was used up in the first stage of the oxidation of 20 ml. of the stock indicator solution, whereas the amount of ferrous solution necessary for the back titration of the green was equivalent to only 1.1 ml., and the quantity theoretically required upon the assumption that the reagent was pure diphenylbenzidine decasulfonic acid was 1.48 ml. The volume of dichromate consumed varied somewhat in the series of experiments, but the amount of ferrous solution required for the reduction of the green remained remarkably constant. Indeed, a portion still needed 1.1 ml. of ferrous solution for back titration after standing for one month in the normal sulfuric acid solution. It would appear that part of the diphenylbenzidine sulfonic acid was oxidized in an irreversible way, but that the green intermediate product itself was very stable.

The potentials observed during a typical titration of this sort are given in Table I, in comparison with the calculated values which should be obtained according to the semiquinone and meriquinone theories, respectively (see also

Fig. 1). In each experiment, 20 ml. of the 0.1% water solution of diphenylbenzidine sulfonic acid was treated with 50 ml. of 1.5 *N* sulfuric acid and 2.0 ml. of 0.01 *N* potassium dichromate in 1.0 *N* sulfuric acid. The potential of the mixture rose gradually during the establishment of equilibrium over a period of twenty to thirty minutes, at the end of which time 5.0 ml. of C. P. 48% hydrofluoric acid was added, and the back titration begun with 0.01 *N* ferrous solution in 1.0 *N* sulfuric acid. Thus the sulfuric acid concentration was approximately 1.0 *N* and constant throughout the titration. The system was allowed to come to equilibrium after the addition of each drop of reducing solution, the whole experiment requiring several hours.

It will be seen from an examination of the data in Table I that the experimental values agree quite well with those calculated on the assumption that the green compound is a semiquinone; they disagree with those calculated for a meriquinone. In the upper part of the curves, the observed values are higher than the calculated ones for a semiquinone, which is what we would expect if there were some overlapping of the first and second stages of the oxidation. Hence, the evidence points quite definitely to the existence of a semiquinone as an intermediate product in the oxidation of benzidine derivatives, rather than to a meriquinone.

TABLE I

(1.47×10^{-5} mole of diphenylbenzidine sulfonic acid in 70 ml. of 1.0 *N* sulfuric acid, and 2 ml. of 0.01 *N* $K_2Cr_2O_7$ in 1.0 *N* sulfuric acid; 5 ml. of 48% C. P. hydrofluoric acid added after thirty minutes, and back titration begun with 0.01 *N* ferrous solution in 1.0 *N* sulfuric acid; potentials referred to satd. calomel electrode.)

% oxidized	Volume, ml.	E. m. f., v. Obsd.	E. m. f., v. Calcd. as meriquinone	E. m. f., v. Calcd. as semiquinone
18.2	78.2	0.3649	0.3793	0.3658
27.3	78.1	.3793	.3876	.3794
36.4	78.0	.3905	.3948	.3904
45.5	77.9	.4005	.4017	.4003
54.6	77.8	.4093	.4088	.4097
63.6	77.7	.4195	.4166	.4196
72.7	77.6	.4331	.4258	.4306
81.8	77.5	.4555	.4379	.4442

$E_{\text{S.Q.}} = 0.405 + 0.06 \log (X/(100 - X))$, where X equals percentage of D. B. oxidized. $E_{\text{M.Q.}} = 0.294 + 0.03 \log [\text{M. Q.}]/[\text{D. B.}]^2$.

As regards the second stage of the oxidation (from green to violet), the experimental results were much less satisfactory. First, the oxidation potential of the potassium dichromate was not high enough to ensure complete conversion of the green intermediate product to the violet holoquinoid form, and, second, more energetic oxidizing agents caused a marked decomposition of the latter, accompanied by drifting potentials. The result was that the quantity of the violet form found varied from experiment to experiment, and only rarely approximated to that consistently found for the green. However, even though the experimental conditions were so unfavorable, the observed potentials always lay closer to the values calculated on the basis of the semiquinone theory than to those required by the semiquinone theory.

Summary

Diphenylbenzidine decasulfonic acid has been oxidized to the corresponding green and violet forms, and the subsequent reduction studied electrometrically. The green form was very stable, the violet considerably less so, and both were reasonably soluble in water and dilute acid solutions. The form of the titration curves indicated that the green intermediate product was a semiquinone, not a meriquinone.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON, AND THE GEORGE WASHINGTON UNIVERSITY]

The Apparent Volumes and Thermal Expansions of Certain Salts in Aqueous Solution between 20 and 40°[1]

BY R. E. GIBSON AND JOHN F. KINCAID

In the course of a study of the correlation of the compressions with other thermodynamic properties of solutions we found it necessary to obtain reliable values of the thermal expansions. For a few aqueous salt solutions these quantities could be computed from measurements already published but the general result of a careful survey was the discovery of an almost complete absence of reliable systematic data. Interest in thermal expansions is enhanced by the researches of Gucker,[2] who found that when the apparent molal expansibilities of electrolytes in aqueous solutions are plotted against the square root of the volume concentration straight lines are obtained, but that the slopes of these lines depend markedly on the individual characters of the salts and are negative instead of positive as an extrapolation of the interionic attraction theory would require. It seemed desirable, therefore, to determine some expansions

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(1) Part of this work is taken from a thesis presented by John F. Kincaid to the George Washington University in partial fulfilment of the requirements for the degree of Master of Arts.

(2) F. T. Gucker, Jr., THIS JOURNAL, **56**, 1017 (1934).

of solutions experimentally so that data on a fair number of typical salts might be available. Accordingly we shall present and discuss in this article the thermal expansions between 20 and 40° of aqueous solutions of barium chloride, potassium bromide, sodium iodide, potassium nitrate and lithium bromide, together with the specific volumes of solutions of the three last-named salts.

Experimental.—Two pycnometers were used in the determination of the specific volumes of the solutions at 25°. They were both of the same design, one being the pycnometer which has been in use in the Geophysical Laboratory for over fifteen years[3] and the other a copy recently made. The volume of the first pycnometer has remained the same, 55.0368 ml. at 25°, for many years; the volume of the second was determined at intervals during the work by weighing its water content. In all, six measurements were made, the mean value being 52.5994 ml. with an average departure from the mean of 2×10^{-4} ml. The thermostats were held at 25.00 ± 0.01°, the temperature being measured with the 10 junction copper–constantan thermoelement already described[4] and a Wolff potentiometer.

The expansions were measured with a dilatometer which, together with the technique, has already been described.[4] The volume of the dilatometer at 25° was redetermined and found to be 47.52 ml. and the capillary was very completely calibrated with weighed threads of mercury. The temperature of the dilatometer thermostat was measured on the Wolff potentiometer with a 5-junction copper-constantan thermoelement, calibrated at the inversion point of sodium sulfate decahydrate (32.384°, 6463 microvolts). The departure from Adams' table[5] at this point was 1.5 microvolts. Temperatures were therefore converted from microvolts to degrees with the aid of this table and a deviation curve. From the change in height of the meniscus of the liquid in the dilatometer capillary, a knowledge of the stem temperature, the expansion of the glass, the cross section of the capillary, the volume of the dilatometer, and the specific volume of the solution, it was possible to compute directly $\Delta_T v$, the change in specific volume of the solution for any finite change of temperature. Readings were taken at even intervals of 2.5°.

Materials.—Each solution was made up separately from weighed amounts of anhydrous salt and distilled water. *Potassium bromide, potassium nitrate, sodium iodide* and *barium chloride* were all obtained from the J. T. Baker C. P. analyzed preparations. *Potassium bromide* and *nitrate* were recrystallized in the ordinary way from water and dried in an oven for several days. Three solutions of approximately 10% were made up with the commercial and the recrystallized potassium nitrate. When interpolation to the same concentration was made, the densities of these solutions departed on an average 0.2×10^{-5} from the mean value. *Sodium iodide* was crystallized from water at a temperature above the decomposition point of the dihydrate, from absolute methanol solution, and was also used without recrystallization. In all cases the solid was powdered and heated for several days around 200°. The solutions were made up and stored in an atmosphere of nitrogen. The densities of concentrated solutions were independent of the sample and it was judged that the salt as obtained commercially was sufficiently pure. *Barium chloride* dihydrate was dehydrated in an Abderhalden apparatus and also in an air oven. No decomposition of the chloride was observed. J. T. Baker C. P. analyzed lithium carbonate and hydrobromic acid were used in the preparation of *lithium bromide.* The former was washed many times with hot distilled water, dissolved in the acid and the alkaline solution was boiled down, filtered, acidified and allowed to deposit crystals of the dihydrate. These were filtered by suction and recrystallized. Two portions were recrystallized five times. The dihydrate was then dried in a vacuum desiccator over phosphorus pentoxide where it was converted to a mixture of the monohydrate and the anhydrous salt. It is of interest to note that, whereas lithium bromide dihydrate loses water at an exceedingly slow rate, if at all, when placed *in vacuo* over "Anhydrone," it loses water rapidly under the same conditions over phosphorus pentoxide. The final dehydration was carried out in the flasks in which the actual solutions were made up. The salt was heated to constant weight in a high vacuum at 100–120° with phosphorus pentoxide absorbing the evolved water. Anhydrous lithium bromide and lithium bromide dihydrate are both extremely hygroscopic.

Two solutions of approximately 10% lithium

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(3) R. E. Hall, *J. Wash. Acad. Sci.*, **14**, 167 (1924).

(4) R. E. Gibson, *J. Phys. Chem.*, **31**, 496 (1927).

(5) "International Critical Tables," Vol. I, p. 58.

bromide and two of approximately 40% lithium bromide were made from entirely different samples and their specific volumes compared. They were consistent to 1 × 10^{-5} and we feel that the purity of the solid lithium bromide justifies specific volumes given to five decimal places.

The experimental results are recorded in the first two tables.[6] Table I gives the specific volumes at 25° and is self-explanatory. Table II gives the changes in specific volume resulting from a temperature change from 25.00° to the temperature indicated together with the corresponding change in apparent volume and the residuals which indicate the consistency of the results and the fit of the equation used to represent the data.

TABLE I

SPECIFIC AND APPARENT VOLUMES AT 25.00°. EXPERIMENTAL RESULTS AND CALCULATIONS

$100\ x_2$	v	ϕ_2	Deviation ($v_{\text{obsd.}} - v_{\text{calcd.}}$) × 10^5 Eq. 1	Eq. 3
		Potassium Nitrate		
0.000	1.00293	(0.377)		
5.361	0.97032	0.3947	1.2	1.3
9.963	.94295	$.4008_8$	−0.4	−0.3
10.132	.94195	$.4011_1$	− .2	− .1
10.300	.94096	$.4012_6$	− .7	− .7
15.243	.91207	$.4068_8$	− .6	− .6
15.289	.91181	$.4069_6$	− .2	− .2
20.423	.88227	$.4121_3$	.6	.6
25.355	.85429	$.4166_8$	.5	.0
		Sodium Iodide		
				Eq. 2
0.000	1.00293	(0.234_1)		
5.378	0.96189	.2399		− 0.2
6.017	.95704	.2403		+ .4
9.287	.93224	$.2417_4$		− .7
10.016	.92673	$.2421_0$		− .3
16.172	.88026	$.2443_7$		− 1.9
19.740	.85346	$.2457_4$		+ 0.6
24.718	.81617	$.2473_5$		+ 1.2
32.047	.76148	$.2495_1$		− 0.6
34.424	.74389	$.2504_4$		+ 7.2
37.636	.72002	$.2512_2$		+ 1.1
43.431	.67718	$.2528_8$		− 1.3
44.546	.66904	$.2534_0$		+ 7.0
48.176	.64225	$.2542_6$		− 4.3
49.707	.63106	$.2548_0$		− 1.0
50.483	.62539	$.2550_8$		+ 0.5
60.020[a]	.55580	$.2579_6$		−15.6
		Lithium Bromide		
0.000	1.00293			
4.989	0.96724_0	0.2874_2		
10.518	$.92816_3$	$.2920_3$		
10.633	$.92735_6$	$.2921_5$		
14.758	.89850	$.2953_0$		
15.007	.89678	$.2956_0$		
19.947	.86240	$.2983_9$		
25.221	.82590	$.3010_2$		
36.962	.74494	$.3049_3$		
39.375	.72822	$.3052_4$		
39.918	.72443	$.3052_5$		
44.980	.68910	$.3052_2$		
54.980	.61797	$.3027_5$		
60.551	.57782	$.3008_5$		

[a] Not used in fitting equation.

TABLE II

THE EXPANSIONS AND APPARENT EXPANSIONS OF AQUEOUS SOLUTIONS OF CERTAIN SALTS

Temp., °C.	$\Delta_T v \times 10^5$	$\Delta_T \phi_2 \times 10^5$	Deviation ($\Delta_T v_{\text{obsd.}} - \Delta_T v_{\text{calcd.}}$) × 10^5
	Potassium Bromide		
	$x_2 = 0$		
20.00	−116.4		
22.50	− 61.4		
25.00	0.0		
27.50	+ 67.5		
30.00	140.8		
32.50	219.8		
35.00	304.1		
37.50	393.6		
40.00	488.0		
	$x_2 = 0.05721$	$v(25°) = 0.96237^a$	
20.00	−131.4	−379	−0.1
22.50	− 68.0	−177	+ .3
25.00	0.0	0	.0
27.50	+ 72.7	+159	− .4
30.00	150.9	318	+ .1
32.50	233.3	456	+ .1
35.00	319.8	579	+ .2
37.50	410.1	682	− .1
40.00	504.5	776	.0
	$x_2 = 0.10465$	$v(25°) = 0.9292_2{}^a$	
20.00	−141.0	−352	−0.2
22.50	− 72.6	−168	+ .2
25.00	0.0	0	+ .2
27.50	+ 76.2	+151	− .2
30.00	157.3	298	+ .2
32.50	241.4	426	+ .1
35.00	328.6	538	− .4
37.50	420.1	647	+ .1
40.00	514.2	739	+ .1
	$x_2 = 0.20357$	$v(25°) = 0.8611_2{}^b\ (0.8611_0{}^a)$	
20.00	−153.3	−297.7	−0.3
22.50	− 77.9	−142.5	+ .3
25.00	0.0	0.0	+ .3
27.50	+ 80.2	+129.7	− .3
30.00	163.9	254.5	+ .1

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(6) The symbols used in this paper are as follows. The subscripts 1 and 2 refer to the water and salt in solution, respectively, the subscripts w and s stand for pure water and pure solid salt, respectively. The symbol Δ_T indicates the increase with temperature of the quantity to which it is prefixed. The weight fraction is represented by x, the grams per cc. by c, the moles per liter by C, the specific volume by v, the apparent volume by ϕ, the temperature in °C. by t. $\phi_T = (\mathrm{d}\phi_2/\mathrm{d}T)_P$ and M is the molecular weight. The apparent volume is defined by the relation $v = x_2\phi_2 + x_1 v_w$.

TABLE II (*Continued*)

Temp., °C.	$\Delta_T v \times 10^5$	$\Delta_T \phi_2 \times 10^5$	Deviation ($\Delta_T v_{\text{obsd.}} - \Delta_T v_{\text{calcd.}}$) $\times 10^5$
32.50	250.0	367.9	+0.1
35.00	338.0	470.6	− .0
37.50	427.9	562.0	− .5
40.00	521.0	649.9	+ .3
x_2 = 0.29858 $v(25°)$ = $0.7968_0{}^a$			
20.00	−156.8	−251.9	−0.3
22.50	− 79.2	−120.9	+ .3
25.00	0.0	0.0	+ .1
27.50	+ 81.3	+113.9	+ .2
30.00	164.8	221.0	+ .5
32.50	248.9	317.2	− .1
35.00	334.5	405.9	− .7
37.50	422.3	489.7	− .5
40.00	512.1	568.7	+ .8
x_2 = 0.38908 $v(25°)$ = $0.7365_5{}^a$			
20.00	−154.1	−213.3	−0.1
22.50	− 77.3	−102.3	+ .2
25.00	0.0	0.0	− .3
27.50	+ 79.6	+ 98.7	+ .2
30.00	159.8	189.7	+ .2
32.50	240.8	273.7	.0
35.00	322.4	351.1	− .4
37.50	405.7	424.6	+ .3
Potassium Nitrate			
x_2 = 0.05361			
20.00	−144.9	− 647	−0.2
22.50	− 74.7	− 310	− .2
25.00	0.0	0	.0
27.50	+ 79.8	+ 297	− .1
30.00	164.7	586	+ .4
32.50	252.9	838	− .3
35.00	346.7	1099	+ .4
37.50	442.7	1309	− .8
40.00	544.7	1546	+ .4
x_2 = 0.10300			
20.00	−163.2	− 571	−0.3
22.50	− 83.0	− 271	+ .5
25.00	0.0	0	− .3
27.50	+ 88.3	+ 270	+ .1
30.00	180.1	522	.3
32.50	274.8	753	− .4
35.00	373.2	975	− .3
37.50	475.0	1183	− .3
40.00	580.1	1383	+ .3
x_2 = 0.15289			
20.00	−176.8	− 511.5	0.0
22.50	− 90.7	− 253.1	− .3
25.00	0.0	0.0	+ .3
27.50	+ 93.4	+ 236.8	+ .3
30.00	189.9	461.8	+ .2
32.50	289.1	673.0	− .1
35.00	391.1	873.2	− .4
37.50	496.0	1063.5	− .3
40.00	604.0	1246.7	+ .4
x_2 = 0.20423			
20.00	−185.9	−456.8	−0.2
22.50	− 94.1	−221.3	+ .3
25.00	0.0	0.0	+ .3
27.50	+ 96.4	209.1	− .2
30.00	195.7	409.8	− .2
32.50	297.7	601.3	+ .1
35.00	401.0	778.5	− .3
37.50	507.3	950.4	+ .3
x_2 = 0.25355			
22.50	− 95.5	−196.0	+0.3
25.00	0.0	0.0	− .4
27.50	+ 98.7	+190.5	− .3
30.00	200.1	374.7	+ .5
32.50	302.4	545.5	− .1
35.00	407.0	709.9	− .1
37.50	513.3	865.7	.0
Sodium Iodide			
x_2 = 0.06017			
20.00	−136.1	− 444	+0.1
22.50	− 70.7	− 216	.0
25.00	0.0	0	.0
27.50	+ 74.9	+ 191	− .7
30.00	156.3	399	+ .5
32.50	240.6	565	.0
35.00	329.8	731	+ .3
37.50	422.2	869	− .3
40.00	519.1	1006	.0
x_2 = 0.09287			
20.00	−145.5	−430	−0.1
22.50	− 74.5	−202	+ .4
25.00	0.0	0	+ .3
27.50	79.5	+197	− .3
30.00	163.8	389	+ .5
32.50	251.3	559	+ .3
35.00	341.9	711	− .3
37.50	436.5	856	− .4
40.00	535.3	997	+ .3
x_2 = 0.16172			
20.00	−162.7	−402.5	+0.1
22.50	− 83.1	−195.4	.0
25.00	0.0	0.0	+ .1
27.50	+ 86.3	+183.6	− .1
30.00	175.7	356.8	+ .1
32.50	268.1	518.2	+ .4
35.00	362.5	665.3	− .1
37.50	459.6	802.0	− .1
x_2 = 0.24718			
20.00	−177.1	−362.1	−0.2
22.50	− 89.2	−174.0	+ .4
25.00	0.0	0.0	− .1
27.50	+ 92.3	167.9	+ .2
30.00	186.0	323.6	− .1
32.50	282.1	471.7	+ .1
35.00	379.1	607.6	− .4
37.50	478.8	738.3	+ .3
x_2 = 0.32047			
20.00	−183.7	−326.4	−0.2
22.50	− 91.9	−156.6	+ .5

TABLE II (*Continued*)

Temp., °C.	$\Delta_T v \times 10^5$	$\Delta_T v \times 10^5$	Deviation ($\Delta_T v_{\text{obsd.}} - \Delta_T v_{\text{calcd.}}$) $\times 10^5$
25.00	0.0	0.0	−0.5
27.50	+ 94.9	+152.9	+ .2
30.00	190.1	294.6	.0
32.50	286.6	428.1	− .2
35.00	384.2	554.2	+ .1
x_2 = 0.43431			
20.00	−182.9	−269.9	0.0
22.50	− 92.4	−132.9	− .2
25.00	0.0	0.0	+ .2
27.50	+ 92.9	+125.9	+ .2
30.00	186.2	245.4	− .1
32.50	280.4	359.4	− .3
35.00	375.6	468.8	+ .1
x_2 = 0.60020			
20.00	−157.3	−184.6	+0.1
22.50	− 78.9	− 90.6	.0
25.00	0.0	0.0	− .1
27.50	+ 79.7	+ 87.8	+ .3
30.00	159.0	171.1	− .1
32.50	239.0	251.7	.0
Barium Chloride			
x_2 = 0.05251 $v(25°)$ = 0.9571_4^c			
20.00	−128.3	−343	−0.1
22.50	− 66.7	−162	+0.1
25.00	0.0	0	− .1
27.50	+ 71.3	+139	− .3
30.00	148.0	278	+ .2
32.50	228.7	388	.0
35.00	313.5	484	.0
37.50	402.3	560	− .3
40.00	495.6	632	+ .2
x_2 = 0.10121 $v(25°)$ = 0.91540^c			
20.00	−138.1	−331	−0.1
22.50	− 71.1	−157	+ .1
25.00	0.0	0	− .1
27.50	+ 74.9	+140	.0
30.00	153.6	268	+ .2
32.50	235.6	375	− .1
35.00	320.9	470	− .1
37.50	409.3	548	− .2
40.00	500.8	615	+ .2
x_2 = 0.15322 $v(25°)$ = 0.8712_6^c or 0.8712_8^b			
20.00	−145.5	−306	0.0
22.50	− 74.4	−146	− .1
25.00	0.0	0	+ .1
27.50	+ 77.7	+134	+ .2
30.00	157.8	252	+ .2
32.50	240.2	353	− .3
35.00	325.5	444	− .1
37.50	412.9	520	− .1
40.00	502.7	584	+ .2
x_2 = 0.20102 $v(25°)$ = 0.83129^c			
20.00	−149.3	−280.1	−0.4
22.50	− 75.3	−130.3	+ .6
25.00	0.0	0.0	−0.1
27.50	+ 78.0	+119.9	+ .1
30.00	158.3	227.8	− .4
32.50	241.9	329.8	+ .6
35.00	325.8	411.9	− .2
37.50	411.8	484.0	− .5
40.00	500.5	550.2	+ .4
x_2 = 0.25934 $v(25°)$ = 0.78302^c			
20.00	−151.8	−252.9	−0.3
22.50	− 76.4	−119.1	+ .4
25.00	0.0	0.0	+ .1
27.50	+ 78.9	+111.4	+ .2
30.00	158.8	210.1	− .1
32.50	241.0	301.5	+ .3
35.00	323.3	378.3	− .3
37.50	407.2	446.1	− .6
40.00	493.3	508.6	+ .5
Lithium Bromide			
x_2 = 0.04989			
20.00	−121.1	−210.5	−0.1
22.50	− 62.9	− 92.2	+ .2
25.00	0.0	0.0	− .1
27.50	+ 68.2	+ 82.2	− .1
30.00	141.4	152.3	.0
32.50	219.2	208.5	+ .1
35.00	301.2	246.6	+ .1
37.50	387.9	278.6	+ .2
40.00	477.8	282.6	− .1
x_2 = 0.10633			
20.00	−125.1	−198.4	−0.3
22.50	− 64.4	− 89.3	+ .3
25.00	0.0	0.0	+ .1
27.50	+ 68.6	+ 78.1	+ .1
30.00	141.0	143.0	.0
32.50	217.1	194.7	− .3
35.00	296.7	234.2	− .3
37.50	380.0	266.2	.0
40.00	466.3	284.0	+ .3
x_2 = 0.15007			
20.00	−126.2	−181.9	−0.3
22.50	− 64.5	− 82.0	+ .4
25.00	0.0	0.0	.0
27.50	+ 68.5	+ 74.0	+ .1
30.00	140.2	136.6	+ .2
32.50	214.7	185.9	− .1
35.00	292.1	223.9	− .5
37.50	373.0	256.5	+ .1
40.00	456.1	275.2	+ .2
x_2 = 0.19947			
20.00	−126.6	−167.4	−0.2
22.50	− 64.7	− 77.7	+ .1
25.00	0.0	0.0	+ .1
27.50	+ 67.7	+ 68.7	+ .2
30.00	137.8	125.8	.0
32.50	210.3	172.0	− .3
35.00	285.6	211.6	+ .1
37.50	362.6	238.1	− .1
40.00	442.0	257.2	+ .2

TABLE II (*Concluded*)

Temp., °C.	$\Delta_T v \times 10^5$	$\Delta_T \phi_2 \times 10^5$	Deviation ($\Delta_T v_{\text{obsd.}} - \Delta_T v_{\text{calcd.}}$) $\times 10^6$
	x_2 = 0.25221		
20.00	−126.8	−157.8	−0.3
22.50	− 64.4	− 73.4	− .1
25.00	0.0	0.0	+ .2
27.50	+ 66.6	+ 63.8	+ .2
30.00	135.0	117.8	.0
32.50	205.4	162.6	− .2
35.00	277.3	197.8	− .4
37.50	351.3	226.0	− .1
40.00	426.7	245.0	+ .3
	x_2 = 0.36962		
20.00	−123.8	−136.4	−0.3
22.50	− 62.5	− 64.4	+ .2
25.00	0.0	0.0	+ .4
27.50	+ 62.8	+ 54.7	− .2
30.00	127.5	104.7	+ .1
32.50	192.6	146.1	− .1
35.00	258.2	179.9	.0
37.50	325.1	208.3	.0
40.00	392.4	229.4	+ .3
	x_2 = 0.39375		
20.00	−123.0	−133.1	−0.4
22.50	− 61.7	− 62.2	+ .3
25.00	0.0	0.0	+ .2
27.50	+ 62.7	+ 55.4	+ .1
30.00	126.2	103.6	+ .1
32.50	190.1	144.3	− .5
35.00	255.0	179.3	− .3
37.50	320.5	208.0	.0
40.00	386.3	229.6	+ .2
	x_2 = 0.39918		
20.00	−122.9	−132.8	−0.4
22.50	− 61.8	− 62.4	+ .2
25.00	0.0	0.0	+ .4
27.50	+ 62.4	+ 54.6	+ .2
30.00	125.4	102.2	− .1
32.50	189.3	143.3	− .2
35.00	253.7	177.9	− .3
37.50	318.7	205.9	− .2
40.00	384.4	228.5	+ .4
	x_2 = 0.44980		
20.00	−120.2	−124.9	−0.3
22.50	− 60.2	− 58.7	+ .3
25.00	0.0	0.0	+ .1
27.50	+ 61.1	+ 53.4	+ .3
30.00	122.3	99.6	− .2
32.50	184.3	141.0	− .1
35.00	246.4	175.9	− .3
37.50	308.9	205.2	− .2
40.00	371.9	229.9	+ .4
	x_2 = 0.54980		
20.00	−116.4	−116.4	−0.1
22.50	− 58.2	− 55.7	+ .1
25.00	0.0	0.0	− .1
27.50	+ 58.8	+ 51.7	+0.1
30.00	117.3	98.0	− .2
32.50	176.5	141.0	+ .1
35.00	235.1	178.6	− .2
37.50	293.9	212.3	− .1
40.00	352.6	241.7	+ .1

[a] Specific volumes from the data of Hölemann and Kohner, *Z. physik. Chem.*, **B13**, 344 (1931), interpolated to the desired concentrations by the equations $\phi_2 = 0.28099 + 0.05287x_2^{1/2}/x_1^{1/4}$ and $\phi_2 = 0.28186 + 0.05012c_2^{1/2}$. [b] Our measurement. [c] Specific volumes interpolated by the equation $\phi_2 = 0.11441 + 0.06964c_2^{1/2}$, from the data of Kohner (*Z. physik. Chem.*, **B1**, 447 (1928); Palitsch, *ibid.*, **A138**, 390 (1928); Shibata and Hölemann, *ibid.*, **B13**, 351 (1931)).

Discussion of Results

Apparent Volumes.—The apparent volumes of potassium nitrate in aqueous solutions at 25° are expressible within experimental error over the whole concentration range as a linear function of the square root of the volume concentration, equation (1).

$$\phi_2 = 0.37763 + 0.07164c_2^{1/2} \qquad (1)$$

This same well-known and useful form of equation also represents the apparent volumes of sodium iodide very well in solutions up to 40% but then fails badly. We found that a linear function of the square root of the geometric mean of the weight fraction and the weight ratio, that is, $x_2^{1/2}/x_1^{1/4}$, equation (2), fitted the data over the whole range of concentration much better than the ordinary square root of the volume concentration formula.

$$\phi_2 = 0.23407 + 0.02479x_2^{1/2}/x_1^{1/4} \qquad (2)$$

$$\phi_2 = .37745 + .07242x_2^{1/2}/x_1^{1/4} \qquad (3)$$

Only the point at 60% NaI shows any large departure from the straight line. It should be mentioned that our values of the specific volumes of sodium iodide solutions are the results of two entirely independent measurements made with different samples of salt in different laboratories. The results for potassium nitrate were also well fitted by equation (3), but for certain other salts formulas of the type of equation (2) were not as good as those of the type of equation (1). It must be admitted that no theoretical basis is known as yet for the remarkable way in which the apparent volumes in concentrated solutions are represented by linear functions of the square root of some quantity expressing the concentration, but the practical value of such functions in the handling and checking of data is enormous. The choice of a concentration variable depends on the particular case and is at present justified only by the length of the concentration range over which the linear function fits the data. We have now examples in which each of the variables, x_2, c_2 and $x_2/x_1^{1/2}$, in turn is to be preferred to the other two.

Baxter and Wallace[7] and Geffcken[8] have determined the specific volumes of solutions of sodium iodide at 25°. Our results are in fair agreement with theirs and slightly more consistent.

As has been shown already,[9–11] the square root law breaks down completely for lithium bromide solutions, the apparent volumes passing through a maximum, and our results indicate (see Fig. 1) that even in moderately dilute solutions (5–20%) ϕ_2 does not vary linearly with $c_2^{1/2}$. Special attention was paid to these solutions because of the numerous breaks on the apparent volume–concentration curves at 35° and 200 bars reported by Scott and his associates[10,11] and on similar curves for data at 20° described by Hüttig and Kükenthal.[12] We determined a large number of specific volumes at 25°. The apparent volumes computed from these results varied quite smoothly with the concentration, and when the expansion data were applied we found that the apparent volumes at 35° behaved likewise. These curves are given in Fig. 1. On the same diagram we have plotted the apparent volumes at 35° recalculated from Scott's density data.[10,11] It will be seen that the two sets of results agree quite well in the more concentrated region except for three points which hardly seem consistent with Scott's own data. The conclusion is therefore drawn that the apparent volumes at atmospheric pressure may be represented as a smooth curve when plotted against the concentration and that the assumption of a series of breaks is not necessary. At lower concentrations our results differ markedly from Scott's. We cannot explain this, but we note that in this region our volumes at 25° agree with those of Baxter and Wallace[7] and that the error in thermal expansion from 25 to 35° would have to be of the order of 100% to account for the difference between our values and Scott's. We have also used the expansions to obtain apparent volumes of lithium bromide at 20° and compared these with the apparent volumes computed from Hüttig and Kükenthal's work. The discrepancy is enormous, the curves run parallel but are displaced by an amount which cannot be explained by minor errors in temperature or calibration of weights. As there is certainly not an error of several hundred per cent. in our expansion data we can say that Hüttig and Kükenthal's work disagrees with that of Scott, Baxter and Wallace, and ourselves. Hüttig and Keller[13] published densities of lithium bromide solutions also at 20°. The apparent volumes at 20° calculated from these results lie close to our values for the apparent volumes at 35°.

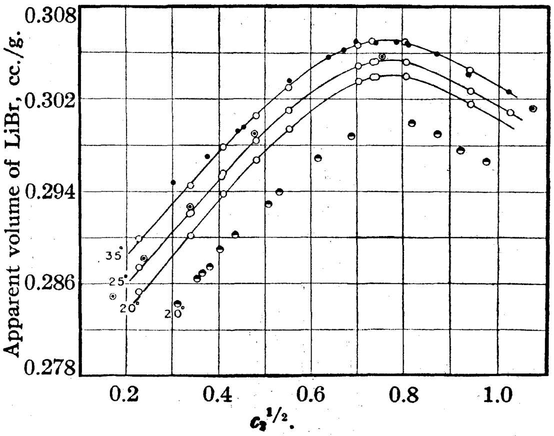

Fig. 1.—The apparent volumes of lithium bromide at different temperatures as functions of the square root of the concentration in grams of lithium bromide per cc. of solution. The results given in this paper are compared with values computed from the work already published. ●, Scott; ◉, Baxter and Wallace; ○, Gibson and Kincaid; ◓, Hüttig and Kükenthal.

Apparent Expansions and Expansibilities.—The apparent expansion $\Delta_T\phi_2$ is the finite change in the apparent volume of the salt corresponding to a finite change in temperature. By the method of least squares quadratic equations of the form

$$\Delta_T\phi_2 = A + B(t - 30) + C(t - 30)^2$$

were fitted to the expansion data for each solution. The values of A, B and C are given in Table III and the fit of the equations may be judged from the residuals in the last column of Table II. When these equations are differentiated, the temperature coefficient of ϕ_2, *viz.*, ϕ_T, is obtainable at any temperature between 20 and 40°. It may be noted that $M_2\phi_T$ is the same as Gucker's[2] (pp. 1018–19) $\Phi(E_2)$. In Fig. 2 we have plotted $M_2\phi_T$ at 25 and at 35° against $C_2^{1/2}$ for the different solutions. The curves for potas-

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(7) G. P. Baxter and C. C. Wallace, THIS JOURNAL, **38**, 70 (1916).

(8) W. Geffcken, *Z. physik. Chem.*, **5B**, 91 (1929).

(9) W. Geffcken, *ibid.*, **155A**, 18 (1931).

(10) A. F. Scott, V. M. Obenhaus and R. W. Wilson, *J. Phys. Chem.*, **38**, 931 (1934).

(11) A. F. Scott and G. L. Bridger, *ibid.*, **39**, 1031 (1935).

(12) G. F. Hüttig and H. Kükenthal, *Z. Elektrochem.*, **34**, 14 (1928).

(13) G. F. Hüttig and M. Keller, *ibid.*, **31**, 390 (1925).

sium nitrate and potassium bromide at 25° are straight lines confirming Gucker's observations, but the curves for these salts at 35° and for the other three salts both at 25 and 35° are distinctly not linear, running in such a way that one may expect a maximum somewhere between the lowest concentration we investigated and the origin. The general shape of these curves is sigmoid, and an examination of Figs. 2 and 3 in Gucker's paper shows that the same is true of the data he examined. It seems probable that in all cases the initial slopes of the apparent expansion–concentration curves are positive in very dilute solution but that they quickly pass through zero and become negative. At higher concentrations the curves have regions of inflection which may be so drawn out that for all practical purposes the curves may be regarded as linear.

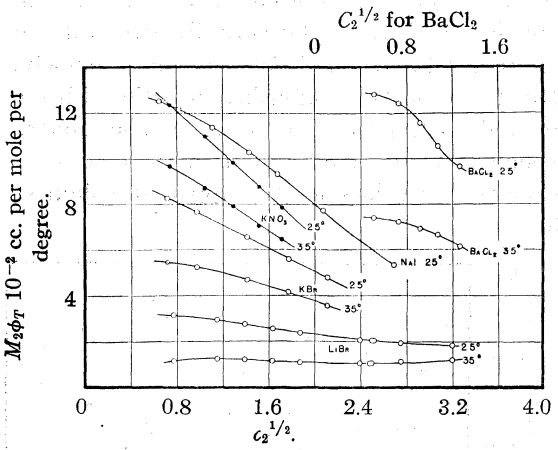

Fig. 2.—The apparent molal expansibilities of salts in aqueous solution at 25 and 35° as functions of the square root of the concentration expressed in moles per liter.

Table III

Coefficients in the Equations Representing the Apparent Expansions as Functions of the Temperature

$$\Delta_T\phi_2 = A + B(t - 30°) + C(t - 30°)^2$$

100 x_2	$A \times 10^5$	$B \times 10^5$	$C \times 10^5$
	Potassium Bromide		
5.721	317.2	57.68	−1.176
10.465	295.6	54.40	−1.018
20.357	254.2	47.22	−0.782
29.858	219.2	40.87	− .613
38.908	189.2	35.12	− .510
	Potassium Nitrate		
5.361	579.3	109.12	−1.323
10.300	518.6	97.41	−1.129
15.289	460.4	87.77	−0.942
20.423	410.6	78.15	− .845
25.355	372.9	70.86	− .684
	Sodium Iodide		
6.017	390.6	72.61	−1.105
9.287	384.2	71.11	−1.016
16.172	356.5	66.52	−0.943
24.718	324.0	60.85	− .766
32.047	294.6	55.25	− .681
43.431	245.7	46.91	− .466
60.020	171.2	32.88	− .271
	Barium Chloride		
5.251	273.9	48.55	−1.302
10.121	266.0	47.16	−1.244
15.322	250.6	44.44	−1.120
20.102	229.8	41.32	−0.946
25.934	210.6	37.92	− .831
	Lithium Bromide		
4.989	153.1	24.70	−1.148
10.633	142.8	23.87	−0.994
15.007	135.6	22.69	− .885
19.947	125.6	21.15	− .806
25.221	117.8	20.03	− .742
36.962	104.4	18.22	− .579
39.375	103.4	18.06	− .549
39.918	102.4	17.97	− .545
44.980	100.0	17.67	− .476
54.980	98.4	17.89	− .358

Although the curve of $M_2\phi_T$ at 25° against $C_2^{1/2}$ is not linear for lithium bromide in aqueous solutions there seems to be no indication of any breaks.

Summary

We have measured the thermal expansions from 20 to 40° of aqueous solutions of barium chloride, potassium bromide, potassium nitrate, sodium iodide and lithium bromide over the entire range of concentration and also the specific volumes at 25° of the solutions of the three last-named salts. From these results apparent volumes, apparent expansions and apparent expansibilities were computed and where possible expressed analytically by simple formulas as functions of temperature and concentration. We have suggested a new concentration variable which sometimes replaces c_2 to advantage in the square root formulas. It seems from our results that the linear relation between apparent expansibilities and the square root of the concentration is fortuitous and not to be expected in general, the complete curve being sigmoid. We find no evidence requiring breaks in the curves of the apparent volumes or the apparent expansions of lithium bromide against the concentration at atmospheric pressure.

Washington, D. C. Received July 23, 1936

[CONTRIBUTION FROM THE LABORATOIRE DE CHIMIE MINÉRALE OF THE COLLÈGE DE FRANCE]

The Ammonolysis of Tantalum Pentachloride

BY HENRI MOUREU AND CLEMENT H. HAMBLET[1]

In a recent note[2] the authors have given evidence that the primary product of the reaction of liquid ammonia on tantalum pentachloride was the heptammine of the trichlorodiamide whose formation was accounted for by the equation

$$TaCl_5 + 17NH_3 \longrightarrow Ta(NH_2)_2Cl_3 \cdot 7NH_3 + 2NH_4Cl \cdot 3NH_3$$

It was found that this compound, on progressive heating to 170° in a vacuum, not only was separated from the ammonium chloride formed in the initial reaction but also underwent loss of the seven molecules of ammonia held by secondary valence.

The trichlorodiamide of tantalum could thus be isolated and its properties studied. Thus, it was possible to show that on heating to 1180° in a current of dry ammonia, the mononitride of tantalum was produced

$$3Ta(NH_2)_2Cl_3 + 8NH_3 \longrightarrow 3TaN + 9NH_4Cl + N_2$$

We have since not only obtained additional data confirming these reactions but have also been able to isolate the pentanitride which is formed at an intermediate stage in this latter reaction and to investigate some previously unrecorded properties of these compounds.

Preparation of Tantalum Pentachloride.—This material was made from tantalum pentoxide by a modification of the method discovered by Demarçay[3] and subsequently used by Ruff and Schiller.[4] The oxide was of high purity, having been separated from columbium pentoxide by fractional crystallization of the potassium heptafluotantalate salt. After three sublimations in a vacuum, the practically colorless pentachloride was collected in small Pyrex tubes which were sealed off. Chlorine analysis of this product, after hydrolysis and separation of tantalum by the method of Hönigschmid and Schlee,[5] showed it to be pure tantalum pentachloride within the limits of the analytical precision. Found: 49.12, 49.31%; calcd., 49.49%.

Formation of $Ta(NH_2)_2Cl_3 \cdot 7NH_3$ by the Action of Liquid Ammonia on Tantalum Pentachloride.—When several volumes of liquid ammonia were condensed on tantalum pentachloride and the mixture allowed to warm up slowly to its boiling point at atmospheric pressure, reaction took place, the heat evolved thereby causing the ammonia to be boiled vigorously, and resulted in the practically complete dissolution of the solid to form a pale greenish-yellow solution.

Evaporation of the ammonia left a residue which was composed obviously of at least two different substances, one white and the other pale yellow, and which continued to evolve ammonia even at room temperature. From the quantity of tantalum pentachloride used and its increase in weight on being treated in this manner, it was ascertained that at 20° between ten and eleven (found: 10.12, 10.70, 10.62, 10.80, 10.34, 10.22) moles of ammonia were fixed per mole of tantalum pentachloride originally taken. It was apparent that the mixture consisted of components at least one of which was unstable.

An attempt to separate the ammonium chloride, for such was presumably the white portion of the residue, from the tantalum compound by extraction with anhydrous methanol, in an apparatus which permitted such an extraction to be carried out at room temperature, was of no avail. Most of the tantalum passed into solution under these conditions and instantly formed a precipitate as the extract was cycled back to the hot alcohol still. This behavior incidentally resembles the action of ethanol on tantalum pentachloride.[6] Extraction of the original material with liquid ammonia left only a small residue which was probably composed of unavoidable hydrolysis products.

Equilibrium Pressure–Composition Measurements.—These experiments were made with the object in view of determining the quantity of ammonium chloride formed by the initial reaction and the total quantity of ammonia fixed using a method similar to that employed by Joannis[7] in his study of the ammonia–boron chloride system. By means of liquid ammonia known quantities of tantalum pentachloride were converted to the mixture just described but instead of allowing the residue to warm up to room temperature, it was maintained at 0° by means of an ice-bath, excess ammonia having been evaporated at a pressure always greater than 1035 mm. which at 0° is the pressure of dissociation of the triammine of ammonium chloride, $NH_4Cl \cdot 3NH_3$, reported by Troost.[8] By measuring equilibrium pressures and volumes of ammonia evolved a series of points on the pressure–composition curve was then determined. Data obtained in three experiments (I, II, III) are tabulated in Table I.

Composition in this table represents the number of molecules of ammonia fixed by the mixture per atom of tantalum present, or x in the over-all formulas $TaCl_5 \cdot xNH_3$ (including ammonium chloride triammine). The values obtained in experiment I, in which measurements were carried down to low pressures during the course of four months, are plotted in Fig. 1, Curve A. It is to be noted that only one well characterized monovariant region of composition can be detected in the curve, that this is at a pressure corresponding

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[1] Recipient of the Moore Traveling Fellowship from the Massachusetts Institute of Technology for the academic year 1934–1935.

[2] Moureu and Hamblet, *Compt. rend.*, **200**, 2184 (1935).

[3] Demarçay, *ibid.*, **104**, 111 (1887).

[4] Ruff and Schiller, *Z. anorg. Chem.*, **72**, 330 (1911).

[5] Hönigschmid and Schlee, *ibid.*, **221**, 129 (1934).

[6] Lindner and Feit, *ibid.*, **132**, 10 (1924).

[7] Joannis, *Compt. rend.*, **135**, 1106 (1902); **139**, 364 (1904).

[8] Troost, *ibid.*, **88**, 578 (1879).

TABLE I

Eq. press., mm.	Compn., x	Eq. press., mm.	Compn., x
I, $TaCl_5$ taken 0.9758 g. ≎ 2.723 millimoles		III, $TaCl_5$ taken 2.3939 g. ≎ 6.6893 millimoles	
1379	17.59	1057.2	16.66
1241	17.59	1040.0	16.36
1153	17.43	1033.9	16.33
1069	17.36	1036.6	16.03
1003	17.01	1030.3	15.69
1018	16.65	1025.8	13.46
1001	16.53	1017.6	11.28
1008	15.22	1006.6	10.94
1021	14.47	922.3	10.75
1003	10.81	816.6	10.70
824	10.59	680.9	10.67
628	10.38	578.4	10.66
433	10.26		
288	10.00		
171	9.61		
88.4	9.23		
48.8	9.11		
7.6	8.49		
2.3	8.34		
1.5	8.28		
0.8	8.23		
0.5	8.18		
II, $TaCl_5$ taken 0.3812 g. ≎ 1.064 millimole		VIII, $TaCl_5$ taken 4.8079 g. ≎ 13.42 millimoles	
1082.6	17.23	884	10.24
1035.4	15.34	704	10.15
1023.3	12.43	527	10.04
927.3	11.06	430	9.96
748.9	10.92	385	9.92
537.3	10.76	334	9.86
454.4	10.62	302	9.80
		290	9.75
		247	9.68
		220	9.57
		176	9.32
		116	9.08
		54	8.82
		12	8.55
		6	8.43

sensibly to that of dissociation of the triammine of ammonium chloride, and that on either side of this region the equilibrium pressure changes abruptly in a linear manner. In fact, as the pressure decreases the composition remains practically constant until a pressure of 300 mm. is reached. Figure 2 shows the data obtained in experiment II in the monovariant region plotted to larger scale.

Equilibrium was only slowly attained, possibly due to the formation of a coating on the surface of the decomposing crystals of reaction product which hindered the diffusion of ammonia out from the undecomposed interior part of the crystals. A similar phenomenon was mentioned by Klemm[9] in the case of the ammines of indium.

In deriving from these curves the amount of ammonia evolved by the triammine of ammonium chloride and the quantity fixed by the solid at the end of this decomposition, the points of intersection of the linear parts of the curve with the theoretical 1035-mm. isobar were used. The results are tabulated in the first three lines of Table II.

TABLE II

Experiment	Initial ammonia	Final ammonia	Difference	Ammonium chloride
I	17.20	10.88	6.32	2.11
II	17.17	11.14	6.03	2.01
III	16.66	10.79	5.87	1.96
IV	...	...	7.34	2.45
V	18.12	10.79	7.33	2.44
VI	19.73	9.93	9.80	3.27
VII	19.79	9.63	10.16	3.39

Initial ammonia content values correspond to the point of commencement of decomposition of the triammine of ammonium chloride and final ammonia content represents the composition when all of the triammine has decomposed. The difference between these quantities divided by three gives the moles of ammonium chloride formed per mole of tantalum pentachloride originally taken.

It can be concluded from these experiments that when liquid ammonia reacts with tantalum pentachloride, two atoms of chlorine in the latter are replaced, forming two molecules of ammonium chloride. Furthermore, the over-all content of ammonia in the mixture obtained after the triammine of ammonium chloride has completely decomposed corresponds to the fixation of eleven molecules per atom of tantalum present. Consequently, each atom of tantalum must be combined with nine atoms of nitrogen, if a mixture of tantalum compounds is not formed which is improbable in view of the duplicatibility of results under different conditions in these three experiments.

Since our analogy with the reaction product of phosphorus pentachloride with liquid ammonia[10] indicates that under these conditions of temperature and ammonia pressure an amide rather than an imide or a nitride is to be expected, the most likely formula that can be assigned to this tantalum compound is that of the heptammine of the

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(9) Klemm, *Z. anorg. Chem.*, **163**, 240 (1927).

(10) Moureu and Rocquet, *Compt. rend.*, **200**, 1407 (1935); *Bull. soc. chim.*, **3**, 829 (1936).

diamidotrichloride of tantalum, formed by the reaction

$$TaCl_5 + 17NH_3 \longrightarrow Ta(NH_2)_2Cl_3{\cdot}7NH_3 + 2NH_4Cl{\cdot}3NH_3$$

Confirmatory evidence for this formula will be presented later in this article under the study of the thermal decomposition of this compound.

It is to be noted that a composition corresponding to the fixation of nine moles of ammonia there is a slight change of curvature, indicating the possible presence of pentammine, $Ta(NH_2)_2Cl_3{\cdot}5NH_3$. This is shown more clearly when plotted to larger scale as in Fig. 1-B. To verify the existence of this compound, equilibrium pressure–composition measurements were carried out at 24.5° on a new sample of the ammine of the diamino trichloride. The results are given in Table I, experiment VIII, and are plotted in Fig. 1-C and Fig. 1-D to larger scale. Although there is a definite change of curvature in this plot, it is so gradual that the point of inflection cannot be ascertained definitely. It is to be observed, however, that this pressure curve intersects the one obtained at 0°, indicating that another phenomenon is taking place. It is probable that slight replacement of more chlorine in tantalum pentachloride occurs at this temperature under an appreciable ammonia pressure. Experiments about to be described bear out this supposition.

It seemed advisable at this stage to investigate the tendency of the remaining three atoms of chlorine still attached to the tantalum to be ammonolyzed off by repeated treatment with liquid ammonia and intermediate heating to various temperatures. Since it was by a procedure similar to this that Schwarz and Jeanmaire[11] succeeded in decomposing an ammonium chloride complex of triamido stannic chloride, it was felt that a further replacement of chlorine in $Ta(NH_2)_2Cl_3{\cdot}7NH_3$ might be accomplished in this manner. This actually did occur, for more than three gram atoms of the original five in the pentachloride were ammonolyzed. The procedure, however led to mixtures and consequently the exact nature of the compounds formed could not be ascertained. Experimental conditions in four experiments (IV, V, VI, VII) are summarized in Table III and the corresponding results are tabulated in Table II.

TABLE III

Experiment	IV	V	VI	VII
Heating temp., °C.	100	100	160	240–250
Time, hrs.	5.5	1	1	1
Times performed	1	4	4	4

It is seen that even heating to 100° causes half an additional gram atom of chlorine to be replaced. This was the justification for the assumption previously made that at 24.5° slow replacement of chlorine occurred which interfered with vapor pressure measurements extending over a period of several months. Furthermore, the number of moles of ammonium chloride formed per mole of tantalum pentachloride originally present increases while the quantity of ammonia fixed after the triammine of ammonium chloride has decomposed increases as the severity of treatment is increased. This is not regular, however, as the results obtained in experiments VI and VII approach similarity even though the temperature to which the mixture has been heated differs by almost 100°. This would seem to indicate the formation of stable tantalum compounds but since the molal quantities obtained differ considerably from whole numbers, it is apparently a question of a mixture of two or more substances, the formulas of which cannot be derived directly from the data.

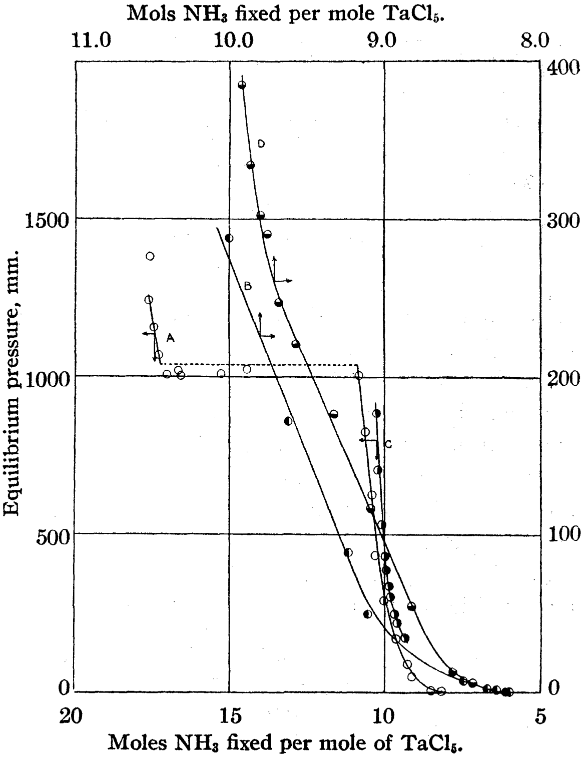

Fig. 1.

Thermal Decomposition of $Ta(NH_2)_2Cl_3{\cdot}7NH_3$.—When the mixture ($Ta(NH_2)_2Cl_3{\cdot}7NH_3$ +

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[11] Schwarz and Jeanmaire, *Ber.*, **66**, 1443 (1932).

$2NH_4Cl$) primarily formed by the action of liquid ammonia on tantalum pentachloride was heated in vacuum, ammonia was evolved continuously as the temperature was raised to 170° and ammonium chloride sublimed onto the cooler parts of the apparatus. At this latter temperature, the evolution of ammonia ceased and hydrogen chloride began to be evolved, showing the commencement of a new reaction. Up to this point seven moles of ammonia had been evolved and two moles of ammonium chloride appeared in the sublimate.

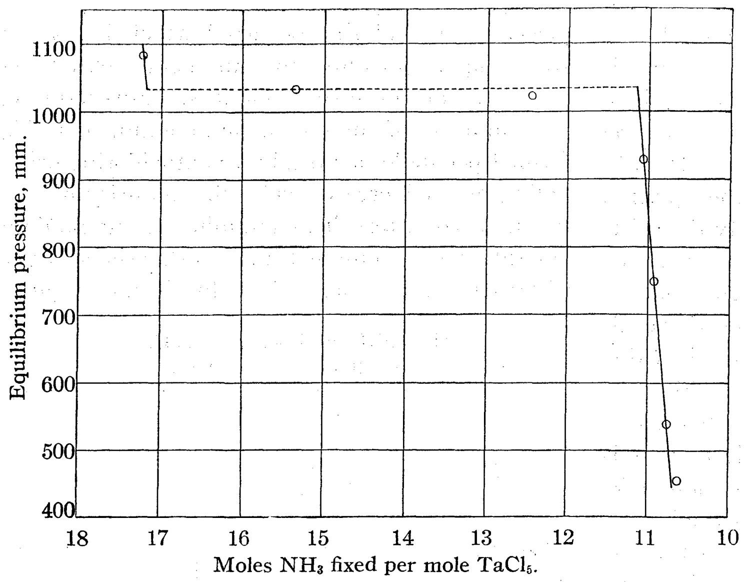

Fig. 2.

As shown by the data in Table IV and by the plot in Fig. 3 there was no indication of a temperature range throughout which there was any discontinuity of evolution, although evolution decreased gradually as the temperature was raised. It is not probable, therefore, that any well-defined intermediate compounds are formed between the heptammine and the amido chloride itself. The data obtained in two experiments are summarized in Table V, all quantities being expressed as total moles per mole of tantalum pentachloride originally present.

TABLE IV

Temp., °C.	NH_3 evolved per mol. $TaCl_5$, mols.	Composition of total solid,[a] x
20–22	2.24	8.72
25–27	2.45	8.51
44–47	3.14	7.82
72–76	4.92	6.04
117	6.03	4.93
170–172	6.62	4.34

[a] Including ammonium chloride.

It is to be noted that although the quantity of ammonia fixed in the end by the tantalum and chlorine (as NH_4Cl) is greater than four by an amount greater than the probable experimental error, nevertheless this deviation was markedly decreased in Experiment II where greater precautions were taken toward the end of the decomposition. Undoubtedly secondary reactions take place to a slight extent with the gaseous ammonia for there was apparently only a very small intermediate temperature range, if any, between cessation of ammonia and commencement of hydrogen chloride evolution, for when the solid residue obtained in expt. 1 was again heated in vacuum to 170°, a small but appreciable hydrogen chloride pressure developed. Another fact which was noted and which undoubtedly did cause a slight error was the formation of a very small quantity of a volatile yellowish tantalum compound of unknown composition which appeared in the sublimate, for a small quantity of white precipitate formed when the latter

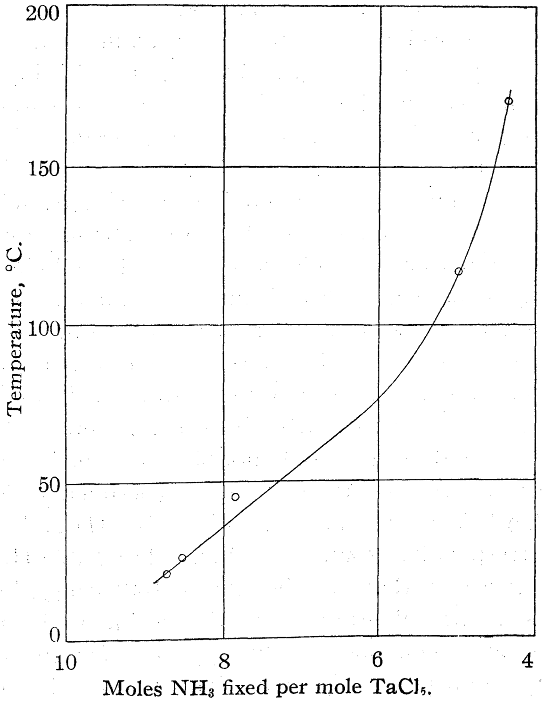

Fig. 3.

Table V

Experiment		I	II
Tantalum pentachloride	g.	5.9847	10.859
	mml.	16.70	30.32
NH_3 initially combined		10.53	6.654
Uncombined NH_3 in apparatus		0.43	Negligible
NH_3 evolved			
(1) Determined gasometrically		6.62	2.50
(2) Determined by direct weighing		6.77	2.52
NH_4Cl sublimed			
(1) From direct weighing		2.04	2.08
(2) From Cl analysis		2.05	2.07
(3) From NH_3 analysis		..	2.08
Final NH_3 content of residue			
(1) From gas evolved		4.34	4.15
(2) From change in wt.		4.19	4.13

was treated with water and was shown to be tantalum hydroxide by microscopic examination of the K_2TaF_7 derivative. However, these factors are both so small that it is felt that they do not seriously impair the conclusions that are to be drawn from these results and are merely suggested as probable explanations of deviations from the main reaction taking place.

The preceding experiments show, then, that when the mixture $[Ta(NH_2)_2Cl_3 \cdot 7NH_3 + 2NH_4Cl]$ undergoes thermal decomposition, no further replacement of chlorine occurs, provided that the ammonia evolved be removed from the system. The ammonium chloride present sublimes off unchanged and the seven molecules of ammonia coordinately bound are evolved completely.

$$Ta(NH_2)_2Cl_3 \cdot 7NH_3 + 2NH_4Cl \longrightarrow Ta(NH_2)_2Cl_3 + 7NH_3 + 2NH_4Cl$$

The composition of this residual tantalum compound was confirmed by analysis.

Analysis of $Ta(NH_2)_2Cl_3$.—The residue in the flask was found to react vigorously with water with evolution of hydrogen chloride and consequently could not be allowed to be exposed to the atmospheric moisture. To determine *nitrogen* content, samples were decomposed with concentrated sulfuric acid, in which reagent gentle heating caused complete dissolution. The ammonia was distilled off from the alkalinized solution and titrated. *Chlorine* was determined by dissolving samples in 33% potassium hydroxide solution (evolution of ammonia), cautious neutralization with nitric acid after dilution, and immediate precipitation of tantalum hydroxide by means of an excess of ammonium hydroxide. The hydroxide was filtered off and washed with dilute ammoniacal ammonium nitrate solution, and chloride in the filtrate determined as silver chloride. Due to occlusion of chloride ion by the colloidal hydroxide[5] it was found helpful, to obtain consistent results, to heat the precipitate of tantalum hydroxide on the water-bath for two days before filtration. *Tantalum* was determined by the method employed by Hahn and Putter,[12] which consisted in treatment of the sample with an excess of sulfuric acid in a weighed platinum crucible and careful evaporation to dryness, the ignited residue being weighed as Ta_2O_5.

Experiment	I	II	Calcd. for $Ta(NH_2)_2Cl_3$
Nitrogen, %	8.8	8.15	8.77
	8.9	8.32	
Chlorine, %	32.86	32.88	33.31
	33.04	33.52	
Tantalum, %	56.40	56.77	56.65
	56.62	56.82	

Due to the fact that the substance could not be ground up and mixed to obtain a homogeneous mixture, the analytical results vary slightly. Taking into consideration this factor along with the fact that any impurities introduced were accumulated in the residue along with incidental hydrolysis products from which purification could not be made at any step of the synthesis, the concordance of the results with the theoretical is satisfactory.

Properties of $Ta(NH_2)_2Cl_3$.—The diamido trichloride of tantalum obtained in this manner is a light yellow solid which decomposes on heating above 170° in vacuum. It is decomposed rapidly by moisture and reacts vigorously with water with evolution of hydrogen chloride and precipitation of hydrated tantalic oxide. That this precipitate contained only negligible quantities of nitrogen was demonstrated by ammonia analysis of its solution in concentrated sulfuric acid. Hence, the hydrolysis can be represented by the equation $2Ta(NH_2)_2Cl_3 + (x + 5)H_2O \longrightarrow Ta_2O_5 \cdot xH_2O + 2HCl + 4NH_4Cl$. When fused with potassium hydroxide, ammonia is evolved and the melt is totally soluble in water. On gentle heating, the diamido trichloride dissolves in concentrated sulfuric acid with liberation of hydrogen chloride. Both of these reactions are in accordance with the above hydrolysis and known properties of tantalic oxide.

Conversion of $Ta(NH_2)_2Cl_3$ to Ta_3N_5.—The more easily prepared ammine–ammonium chlo-

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(12) Hahn and Putter, *Z. anorg. Chem.*, **127**, 153 (1923).

ride mixture was employed in one experiment. It was heated continuously in the ammonia current at 750° for six days, at which time the sublimation of ammonium chloride to the cooler parts of the tube had ceased. The non-volatile residue remaining in the boat was red with a few purple spots. It was analyzed by the methods described for the diamide. Chlorine was not present. The data are summarized in Table VI.

TABLE VI

			Calcd. for Ta_3N_5
Solid reactant, g.	2.6886		
Ta_3N_5, g.	1.0780		
Ta in Ta_3N_5, %	87.41	88.00	88.57
N in Ta_3N_5, %	11.16	10.97	11.43
Average % Ta	87.39		
Average % N	11.06		
Total % found	98.45		
Atomic ratio of N/Ta	1.640		1.667

The pure diamide gave similar results. At 650–670° the product obtained was brighter red, more homogeneous in appearance and contained no dark spots. The variation of the analytical results among themselves is due to lack of homogeneity as the product was not ground up before analysis. The sum of the percentages of tantalum and nitrogen lacks 1.55% of being 100. Oxide formed from unavoidable reaction of the initial reactants with moisture of the air during experimental manipulation before the conversion is doubtless partly the cause of this discrepancy. The ratio N/Ta is somewhat better than the only other value found in the literature. Joly[13] prepared tantalum pentanitride directly by the action of gaseous ammonia on tantalum pentachloride at elevated temperature and found the corresponding ratio in his product to be 1.61.

It is to be concluded that when the diamido trichloride of tantalum, or its ammine, is heated in a current of ammonia, all of its chlorine is evolved as ammonium chloride which sublimes off and leaves a residue consisting essentially of the red pentanitride of tantalum. Its formation is accounted for by the equation

$$3Ta(NH_2)_2Cl_3 + 8NH_3 \longrightarrow Ta_3N_5 + 9NH_4Cl$$

Physical Properties of Ta_3N_5.—Although the X-ray spectrum of tantalum mononitride is known and the compound has been found to be crystalline,[14] the corresponding data for the pentanitride are lacking. On submitting the latter to X-ray analysis, it showed several well-defined, characteristic lines which were different from those of the mononitride later prepared. Hence, it is to be concluded that the pentanitride is also crystalline. Its density was found to be 8.5 and it was slightly diamagnetic.

Conversion of $Ta(NH_2)_2Cl_3$ **to TaN.**—Joly[13] found that the pentanitride was converted to the black mononitride by heating in a current of ammonia to red heat. The same conversion takes place as an intermediate step if the diamido trichloride or its ammine be treated similarly as we have already shown in the previous paper.[2] We have evidence that this step consists merely in the decomposition of the pentanitride, the presence of ammonia having no essential bearing on the reaction, which goes according to the equation

$$Ta_3N_5 \longrightarrow 3TaN + N_2$$

The conversion from the ammine was carried out in the same manner as for the pentanitride but at a higher temperature. A 2.1-g. sample of the mixture obtained by the action of liquid ammonia on tantalum pentachloride was heated in a current of dry ammonia gas at 1190° for twenty-four hours. Even under these conditions the conversion was not complete for the black residue obtained still contained more than theoretical nitrogen as shown by the following analysis which was carried out in the manner described for the pentanitride. No chlorine was found to be present.

	Found		Calcd. for TaN
Tantalum, %	91.61	91.75	92.81
Nitrogen, %	8.34	8.11	7.18

When heated in a vacuum the red pentanitride, made from $Ta(NH_2)_2Cl_3$ by heating in a current of ammonia at 750°, evolved nitrogen at 730°. A certain amount of hydrogen, however, was given off simultaneously (0.218 mole per mole of Ta_3N_5), indicating that the initial material contained a hydrogen compound, perhaps a small quantity of an imide, which underwent a decomposition similar to that observed by Moureu and Wetroff[15] in the case of phosphorus compounds. On the other hand, analysis of the black product obtained showed it to contain 8.01% nitrogen and the amount of nitrogen evolved corresponded to only 78% of the theoretical amount for formation of TaN even after six hundred hours of heating in vacuum at 800–850°. It appears that at these temperatures transformation of the pentanitride in vacuum is very slow.

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(13) Joly, *Compt. rend.*, **82**, 1195 (1876).

(14) Van Arkel, *Physica*, **4**, 294 (1924).

(15) Moureu and Wetroff, *Compt. rend.*, **201**, 1381 (1935).

Thermal Decomposition of $Ta(NH_2)_2Cl_3$ in Vacuum.—Due to the complicated character of this reaction it was not possible to arrive at any definite conclusions concerning its mechanism although it can be said with certainty that the two nitrides mentioned are among the products. The main reaction involved seems to be the following, although the change is evidently much more complicated.

$$3Ta(NH_2)_2Cl_3 \longrightarrow Ta_3N_5 + NH_4Cl + 8HCl$$

When heated in vacuum the first gaseous product, hydrogen chloride, commenced to be evolved at 170°. Ammonium chloride sublimed to the cooler parts of the apparatus along with a yellow to green tantalum compound which decomposed with evolution of hydrogen chloride and formation of a dark green to black compound on heating with a free flame. As shown by the data summarized in Table VII for experiments in which samples of the diamido trichloride were heated to various temperatures in vacuum and the residues obtained analyzed, temperatures as high as 800° are required to expel the chlorine completely.

TABLE VII

Experiment		(A)	(B)	(C)	(D)
Temp. of decomposition, °C.		400	600	600	800
Time of decomposition		Several days	3–4 hrs.	2 days	5–6 hrs.
Wt. of sample, g.		1.1006	1.5353	0.4616	1.6080
Millimoles $Ta(NH_2)_2Cl_3$		3.447	4.808	1.445	5.036
Millimoles HCl evolved		1.82	....	1.47	6.80
Millimoles N_2 evolved		0.00	....	0.08	0.31
Wt. of residue, g.		0.7169	0.8938	0.2005	0.7324
Composition of residue, %	Ta	75.3	80.33	....	86.12
			78.98		86.12
	N	6.8	7.12	9.80	10.03
			7.04		10.01
	Cl	16.5	5.90	3.4	0.0
			5.81		

The residue obtained varied from greenish brown to black as the temperature of decomposition was raised. In all cases, however, sulfur dioxide was liberated from concentrated sulfuric acid in the nitrogen analysis while the dissolving solid became bright red in experiments (B), (C) and (D), indicating that a superficial coating of mononitride hid the color of the pentanitride. That pentanitride actually was the chief component of the residue in experiment IV was confirmed by its X-ray spectrum. Although the other residues failed to show clearly defined lines, in the latter case well-defined lines corresponding in position to those previously obtained from the pentanitride were found.

The composition of the volatile tantalum compound could not be ascertained because of its small quantity and because of its rapid decomposition by the moisture of the atmosphere. Due to the fact that it underwent a color change on heating it could not have been tantalum pentachloride.

Magnetism of Tantalum Pentachloride.—It might be supposed that the difference in reactivity of the chlorine in tantalum pentachloride to liquid ammonia might be due to dissimilarity in bonding, for example the attachment of three chlorine atoms by doublets, while that of the remaining two by singlets with the formation of an octet structure around the tantalum. In this case it was to be expected that the pentachloride would be paramagnetic. Actual determination of the magnetism of iron-free pentachloride, however, showed it to be slightly diamagnetic. An average of three determinations made on a Curie balance in which the pentachloride was both packed and fused in the determination tube gave for x the value $-0.231 \pm 0.002 \times 10^{-6}$. Hence some other explanation must be sought for this difference in reactivity.

Discussion

Schwarz and Jeanmaire[11] found that with the normal valence halides of Group IV of the periodic classification those of the more metallic high atomic weight elements differed considerably from those of less metallic low atomic weight elements in the ease with which chlorine atoms were ammonolyzed by liquid ammonia. While the tetrahalides of silicon and germanium suffered complete ammonolysis, that of tin required special treatment to bring about complete replacement of chlorine and lead tetrachloride formed a stable chloramide, $Sn(NH_2)_3Cl$, which decomposed to a chloronitride, SnNCl. In the reactions of the chlorides of Group V with liquid ammonia there is an analogous behavior: the pentachloride of phosphorus suffers complete ammonolysis[16] while the halides of bismuth, BiX_3, form ammines but are not ammonolyzed.[17] The transitional element, tantalum, on the other hand, has intermediate properties between phosphorus and bismuth and its pentachloride undergoes only partial replacement of chlorine to form an ammoniated diamido trichloride.

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(16) Moureu and Rocquet, *Compt. rend.*, **200**, 1407 (1935).

(17) Schwarz and Striebich, *Z. anorg. Chem.*, **223**, 399 (1935).

Summary

1. From equilibrium pressure–composition measurements it has been shown that the primary product of the action of liquid ammonia on tantalum pentachloride is soluble $Ta(NH_2)_2Cl_3 \cdot 7NH_3$ which is deposited from solution, along with the ammonium chloride simultaneously produced, in the form of a light yellow crystalline mass.

2. When heated in a vacuum this compound first loses its seven molecules of ammonia coördinatively bound to form the yellow diamido trichloride of tantalum. Study of this reaction revealed a slight discontinuity at the point where the total ammonia fixed by the solid material was nine moles per gram atom of tantalum present, indicating the formation of the pentammine of the diamido trichloride.

3. By repeated alternate heating and submission to the action of liquid ammonia more than three of the original five chlorine atoms in tantalum pentachloride can be ammonolyzed off to form a mixture the components of which were of undetermined character.

4. Some properties of $Ta(NH_2)_2Cl_3$ have been described and its thermal decomposition both in the presence of gaseous ammonia and in vacuum studied. In the presence of gaseous ammonia, the first product isolated was the pentanitride while in a vacuum at the same temperature the pentanitride is accompanied by some mononitride and a small amount of a volatile tantalum compound of undetermined composition.

5. At elevated temperature, in either an atmosphere of ammonia or in a vacuum, the pentanitride is found to decompose to the mononitride with the evolution of nitrogen.

6. Tantalum pentanitride has been shown to be crystalline from its X-ray spectrum and its density has been determined.

7. The magnetic constant of tantalum pentachloride has been measured.

WILMINGTON, DEL. RECEIVED JULY 28, 1936

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

The Separation of Gallium and its Colorimetric Determination by Means of Quinalizarin[1]

BY H. H. WILLARD AND H. C. FOGG[2]

Practically the only method available for the detection and estimation of small amounts of gallium is by means of the spectroscope. This furnishes a specific and sensitive method for detection, and one which in the hands of experienced manipulators is quite accurate for its determination. However, it has the disadvantages of requring an apparatus which not all laboratories possess, and a technique which everyone has not had an opportunity to develop.

Dennis and Bridgman[3] using a spark were able to detect, by means of a direct vision spectroscope, the gallium line, 4172, in a concentration of 3 mg. of gallium per 100 ml. when 0.15 ml. of the solution, corresponding to 0.0046 mg. of gallium, was placed in the small cup used to hold the solution. Approximately five times this amount of gallium was required for the line 4033 to be visible. The spectrograph has also been employed by Papish and Holt[4] for the direct detection and semi-quantitative estimation of gallium in certain minerals. Kimura, Nakamura and Kusibe[5] combined chemical concentration with the spectrographic method for the qualitative examination of a large number of Japanese minerals for gallium.

A colorimetric method, even if not as specific, is desirable and an investigation was, therefore, made to find a dye which would form with gallium, a suitable lake.

Experimental

Aurin tricarboxylic acid, alizarin red-S, titan yellow and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) were tried. Although the first dye gave a color with small amounts of gallium, as stated by Corey and Rogers,[6] no suitable experimental conditions could be established which would allow an accurate colorimetric determination.

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[1] This manuscript was originally received on August 14, 1933, but was withdrawn and resubmitted after additional experimental work had been done.—EDITOR.

[2] Holder of the J. T. Baker Chemical Company Fellowship in Analytical Chemistry for the Mid-Western Division for the academic year, 1931–1932.

[3] Dennis and Bridgman, THIS JOURNAL, **40**, 1531 (1918).

[4] Papish and Holt, *J. Phys. Chem.*, **32**, 142 (1928).

[5] Kimura, Nakamura and Kusibe, *J. Chem. Soc. Japan*, **52**, 55–62 (1931).

[6] Corey and Rogers, THIS JOURNAL, **49**, 216 (1927).

Alizarin red-S gave a pink to salmon color in buffered solutions. However, the limits of *p*H range, from 4.0 to 4.5, were so narrow and the effect of varying concentrations of buffer salts so great that it was practically valueless as a reagent. Titan yellow gave no color with gallium. Quinalizarin gave a pink to amethyst color, depending upon the concentration of gallium and the *p*H of the solution. Kolthoff[7] has suggested this last reagent as a sensitive test for aluminum.

Preliminary Investigation of Quinalizarin.—This preliminary work showed that: (a) gallium produced a distinct color in the *p*H range of 4.5 to 6.0, and that the most favorable condition, considering the effect of aluminum, etc., was a *p*H of 5.0; (b) the addition of ammonium acetate or ammonium succinate increased the intensity of color of the dye alone and also of solutions containing gallium to about the same extent; (c) the presence of ammonium chloride made the difference in color between the blank and gallium solutions somewhat more pronounced; (d) in general the most uniform results could be obtained if the solutions had a *p*H of 5 and were normal in ammonium acetate and half normal in ammonium chloride.

Action of Quinalizarin with Other Ions.—Qualitative tests in a solution of *p*H 5.0, normal in ammonium acetate and half normal in ammonium chloride showed that: iron (Fe^{+++}), tin (Sn^{++}), antimony (Sb^{+++}), copper (Cu^{++}), lead (Pb^{++}), indium (In^{+++}), germanium (Ge^{++++}), vanadyl (VO^{++}), vanadate (VO_3^{-}) and molybdate (MoO_4^{--}) give colors which are not completely inhibited by fluoride. Iron (Fe^{+++}) and lead (Pb^{++}) cause a blue color while the others are pink. All are very sensitive. Zirconium (Zr^{++++}), thorium (Th^{++++}) and the rare earths give a blue, while tin (Sn^{++++}), beryllium (Be^{++}), aluminum (Al^{+++}), thallium (Tl^{+++}), titanium (Ti^{++++}), arsenite (AsO_3^{---}) and antimonate (SbO_4^{---}) cause a pink color which can be prevented by the addition of fluoride. The alkalies, alkaline earths, magnesium (Mg^{++}), manganese (Mn^{++}), iron (Fe^{++}), mercury (Hg^{++}), thallium (Tl^{+}), cadmium (Cd^{++}), uranyl (UO_2^{++}), tungstate (WO_4^{--}) and arsenate (AsO_4^{---}) give rise to no color. Silver (Ag^{+}), mercury (Hg^{+}), bismuth (Bi^{+++}), tantalum (Ta^{+++++}) and columbium (Cb^{+++++}), either precipitate as chlorides or hydrolyze out, thus causing no interference after removal by filtration. Cobalt (Co^{++}), nickel (Ni^{++}) and chromium (Cr^{+++}) do not interfere except for their own color. Zinc (Zn^{++}) can be present to the extent of 0.5 g. per liter before any color can be seen. More than that gives an amethyst to blue color.

Influence of Various Acid Radicals on the Color Produced by Gallium (Ga^{+++}), Iron (Fe^{+++}) and Aluminum (Al^{+++}).—Citrate, oxalate and tartrate effectively prevented the formation of color in all cases.

Phosphate had no effect on the color produced by aluminum but prevented the color due to ferric iron if added in sufficient concentration. However, it caused a very appreciable decrease in the color given by gallium.

Fluoride effectively prevented the color given by aluminum, while exerting only a relatively small influence in the case of iron and gallium. The only effect with gallium was a slight decrease in the intensity of color in all solutions, including the blank (see Table I). Experiments showed that 0.5 g. of sodium fluoride per liter, in excess of that required to form Na_3AlF_6, was necessary for the complete prevention of lake formation by aluminum. This was also about the maximum concentration of sodium fluoride permissible without seriously decreasing the color caused by gallium.

The Limit of Sensitivity for Gallium, Ferric Iron, Aluminum, Zinc and Indium.—This was determined by comparison of 50 ml. of solution in 50-ml. Nessler tubes, 125 mm. to the mark, the source of light being G. E. daylight bulbs, diffused by a ground glass plate. All solutions were *N* in ammonium acetate, 0.5 *N* in ammonium chloride and had a *p*H of 5.0 ± 0.1 determined with a quinhydrone electrode. One series contained no sodium fluoride while the other contained 0.5 g. per liter. One ml. of a 0.01% alcoholic solution of quinalizarin was added. The figures given below represent the concentrations of the ions which gave sufficient color to be distinguished with certainty from the blank upon repeated determinations.

TABLE I

LIMIT OF DETECTION OF Ga, Al, Fe^{+++}, Zn AND In WITH QUINALIZARIN

Metal	NaF, 0.5 g./l. metal mg./l.	No NaF, metal mg./l.
Ga	0.02	0.02
Al	20.00	.12
Fe (ic)	0.05	.02
Zn	800.00	400.00
In	10.00	2.00

Since it is obvious that a satisfactory colorimetric determination of gallium is possible only after a separation from many other metals, a study of such separations is described in the following pages. The most difficult and important separations, such as those from aluminum, iron and indium, are so different that they must be treated separately. The usefulness of the method is considerably reduced by the difficulty in removing iron, but many cases are encountered in which only very small amounts of iron are present.

The Determination of Gallium in the Presence of Aluminum

The Influence of Various Salts and *p*H on the Separation of Aluminum from Gallium by Means of Sodium Fluoride.—Qualitative and semi-quantitative tests showed that the presence of ammonium chloride, ammonium acetate, the *p*H of the solution at the time of addition of sodium fluoride, the excess of sodium fluoride and the presence of much sodium or potassium salt influenced the separation of aluminum and the recovery of gallium. Extensive experiments showed that the best separation of aluminum, by precipitation as Na_3AlF_6, was obtained when sodium fluoride was added as a saturated solution to the solution containing aluminum and gallium which was about half normal in ammonium chloride and buffered with ammonium acetate to a *p*H of around 5. The presence of more than a few milligrams of potassium or 100 mg. of sodium ion was detrimental to the above separation, although neither potassium nor sodium interfered with the colorimetric part of the determination.

Procedure.—The solution containing gallium and aluminum is neutralized to turbidity with ammonium hy-

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[7] Kolthoff, *Chem. Weekblad*, **24**, 447 (1927); *J. Am. Pharm. Assoc.*, **17**, 360 (1928).

droxide, cleared with 6 *N* hydrochloric acid, and 4 ml. in excess added. This is followed by 7.7 g. of ammonium acetate and 2.7 g. of ammonium chloride. (This will make the solution *N* in ammonium acetate, 0.5 *N* in ammonium chloride, and give a *p*H of nearly 5.0 when finally diluted to 100 ml.) After diluting to 70–80 ml. and heating to 70–80°, enough saturated sodium fluoride solution is added, while stirring, to form Na_3AlF_6 and leave 0.5 g. per liter in excess. The resulting precipitate should be of a fine, crystalline nature. If it is of the opalescent, almost invisible type, some of the gallium is practically certain to be retained or else the aluminum may not be removed entirely. When it has stood for one to one and a half hours, with occasional stirring, paper pulp is added, the precipitate filtered off, the filtrate diluted to 100 ml. and adjusted to a *p*H of 5.0 using a quinhydrone electrode. Aliquot portions of such volume as to contain from 0.001 to 0.01 mg. of gallium are placed in 50-ml. Nessler tubes and filled to the mark with the stock solution from which the standards are made. A series of standards is prepared by adding to 50-ml. portions of this solution in Nessler tubes, definite volumes of a standard gallium chloride solution containing 0.01 mg. of gallium per ml. One ml. of a 0.01% alcoholic solution of quinalizarin is added to each tube, the contents stirred and the colors compared after one or two minutes.

Using 50-ml. Nessler tubes, the best concentration for comparison lies between 0.02 and 0.2 mg. of gallium per liter. Between 0.02 and 0.08 mg. per liter, a difference of 0.01 mg. per liter can be detected easily. Above that, it requires a difference of 0.02 mg. per liter.

The quinalizarin solution is not very stable and becomes practically useless after it has been prepared a week. Neither is it much good directly after preparation. It gives the best results from one to four days after preparation.

It is not necessary that the solutions have a *p*H of exactly 5.0, but it is necessary that both standards and unknown have the same *p*H. A very great deviation from 5 is not recommended, however, since at 4.5 the sensitivity of the gallium is much less, while at a higher *p*H the sensitivity of aluminum is greater.

The presence of 0.5 g. of sodium fluoride per liter is to be recommended in all cases, even if a separation of aluminum has not been made, since it will prevent any color due to traces of that element which are almost certain to be present.

The results shown in Table II, numbers 1 to 10, were obtained by the above method, while numbers 11 to 15 were obtained without preliminary separation of aluminum.

TABLE II

DETERMINATION OF GALLIUM IN THE PRESENCE OF ALUMINUM

No.	Al, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	10	0.000	0.000	±0.000
2	10	.005	.0047	− .0003
3	10	.010	.011	+ .001
4	10	.010	.012	+ .002
5	10	.010	.010	± .000
6	10	.020	.021	+ .001
7	10	.050	.047	− .003
8	20	.000	.000	± .000
9	20	.010	.0075	− .0025
10	20	.010	.006	− .004
	Al, mg./50 ml.	Ga taken, mg./50 ml.		
11	0.75	0.000	0.000	±0.000
12	.75	.0005[a]	.000	− .0005
13	.75	.001	.0011	+ .0001
14	.75	.0025	.0028	+ .0003
15	.75	.005	.005	± .000

[a] 0.0005 mg. of gallium in 50 ml. of solution is beyond the limit of sensitivity of the test.

From this it is seen that gallium can be separated accurately from aluminum if not more than 10 mg. of the latter is present. If the concentration of aluminum is not greater than 15 mg. per liter, the gallium can be determined directly without a preliminary precipitation of aluminum as Na_3AlF_6.

The Determination of Gallium in the Presence of Iron and Indium

Since quinalizarin gives a very sensitive color reaction with ferric iron, it is essential that every trace of this ion be removed before proceeding with the colorimetric determination of gallium. Experiments showed that it was not possible to convert the iron into ferrocyanide and determine the gallium directly, nor to collect quantitatively the latter from a solution by precipitating it along with cadmium sulfide. When the iron was reduced before adding quinalizarin, it was found that the reducing agents such as bisulfite, hydrazine sulfate and hydroxylamine hydrochloride failed to cause complete reduction. Others, like sodium hydrosulfite and phenylhydrazine hydrochloride, destroyed the dye.

The Separation of Iron and Indium from Gallium by Means of an Excess of Sodium Hydroxide.—Although this is a standard method of separation in ordinary analytical work, two serious difficulties were encountered in this instance. First, the adsorptive properties of ferric hydroxide proved to be so great that more than 1 mg. of iron prevented complete recovery of the gallium. Second, sufficient ferric hydroxide to give a color with the dye remained in the colloidal state and passed through the filter, even though the precipitate was settled by centrifuging, and removed by the method recommended by Cox, Schwartze, Hahn, Unangst and Neal,[8] for the separation of iron and aluminum. However, the use of hydrated manganese dioxide as a collector according to the method of Stokes and Cain[9] was found to give entirely satisfactory results for both iron and indium.

Procedure.—The solution containing the iron and gallium in 25 ml. or less, was heated nearly to boiling and enough approximately 3 *N* sodium hydroxide added to make the final concentration between half normal and normal. The heating was continued until the ferric hydroxide had coagulated. Paper pulp was added, the precipitate filtered off and washed with a hot 1% sodium chloride solution made alkaline with sodium hydroxide.

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(8) Cox, Schwartze, Hahn, Unangst and Neal, *Ind. Eng. Chem.*, **24**, 403 (1932).

(9) Stokes and Cain, THIS JOURNAL, **29**, 409 (1907).

The paper pulp and filter paper used in this, and the next, filtration had been treated with hot 1.5 *N* sodium hydroxide solution and then washed with water. The filtrate was heated nearly to boiling, eight to ten drops of a 1% potassium permanganate solution added, and this followed in a minute or two by enough alcohol (5 to 10 drops) to cause reduction. The heating was continued until all green color had disappeared, and the brown precipitate of hydrated manganese dioxide had formed. This was filtered off and washed as before. The filtrate was neutralized to litmus with hydrochloric acid and enough ammonium chloride, ammonium acetate and sodium fluoride introduced so that the *p*H of the solution and the salt concentration would have the values previously recommended, when the whole was diluted to the desired volume (100 or 250 ml.). This was most conveniently done by adding the sodium fluoride as a saturated solution, and the other two salts as a stock solution with a *p*H of 5, which was 1.5 *N* in the former and 3 *N* in the latter.

In the case of indium the precipitate need not be filtered off before adding the permanganate.

The gallium was then determined as described under "The Determination of Gallium in the Presence of Aluminum." Table III shows the results obtained using the above procedure.

TABLE III

THE SEPARATION OF GALLIUM FROM IRON AND INDIUM

No.	Fe, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	0.5	0.010	0.009	−0.001
2	.5	.020	.018	− .002
3	1.0	.000	.000	± .000
4	1.0	.005	.006	+ .001
5	1.0	.020	.020	± .000
6	1.0	.060	.058	− .002
7	2.0	.010	.005	− .005
8	2.5	.010	.008	− .002
9	20.0	.010	.003	− .007
10	0.0	.010	.009	− .001
11	.1	.010	.010	± .000
12	.2	.000	.000	± .000
13	.2	.005	.0055	+ .0005
14	.2	.010	.012	+ .002
15	.2	.050	.048	− .002
	In, mg.			
16	100	.000	.000	± .000
17	100	.010	.011	+ .001
18	100	.025	.028	+ .003
19	100	.050	.052	+ .002
20	100	.060	.058	− .002

In numbers 10 to 20 the precipitate of ferric hydroxide, or indium hydroxide, was not filtered off before adding the potassium permanganate and reducing.

From this it can be seen that gallium can be determined accurately in the presence of iron, using the method given, only when not more than 1 mg. of the latter is present; otherwise a very appreciable amount of the gallium will be lost. Determinations 10 to 15 show that if not more than 0.2 mg. of iron is present, it is unnecessary to filter off the ferric hydroxide before adding the permanganate. With larger amounts of iron, it was found that it was removed incompletely unless filtered off as recommended in the procedure. Indium gives no difficulty even when 100 mg. is present.

Data obtained, but not included in the table, showed that if the concentration of indium did not exceed 8 mg. per liter, accurate determinations of gallium could be made without a preliminary separation.

The Determination of Gallium in the Presence of Zinc and Aluminum or Iron

Since preliminary determinations, Table I, showed that nearly 600 mg. of zinc per liter gave no color with quinalizarin if 0.5 g. of sodium fluoride was present, no special procedure was necessary for determining gallium in the presence of this element.

With zinc alone, the gallium was determined directly in solutions having a *p*H and the salt concentrations previously given. (Results are shown in Table IV, numbers 1 to 5.) When zinc and aluminum were both present, the latter was separated by the procedure given under "The Determination of Gallium in the Presence of Aluminum," and the gallium determined as if zinc were absent. (Determinations from 6 to 11 show the results obtained.) With iron and zinc present the procedure given under "The Determination of Gallium in the Presence of Iron" was followed except that sufficient sodium hydroxide was added to dissolve the zinc hydroxide. (Determinations 12 to 15 are representative of the results obtained.)

TABLE IV

THE DETERMINATION OF GALLIUM IN THE PRESENCE OF ZINC AND IRON OR ALUMINUM

No.	Al, mg.	Zn, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1		25.0	0.000	0.000	±0.000
2		25.0	.001	.0012	+ .0002
3		25.0	.005	.006	+ .001
4		50.0	.010	.010	± .000
5		50.0	.020	.020	± .000
6	10.0	20.0	.000	.000	± .000
7	10.0	10.0	.005	.006	± .001
8	10.0	20.0	.025	.023	− .002
9	0.25	12.5	.003	.0035	+ .0005
10	.25	12.5	.010	.009	− .001
11	.50	20.0	.030	.035	+ .005
	Fe, mg.				
12	1.0	20.0	.000	.000	± .000
13	1.0	20.0	.005	.004	− .001
14	1.0	100.0	.025	.024	− .001
15	1.0	200.0	.060	.065	+ .005

Numbers 4, 5, 10, 11, 14 and 15 were diluted to 100 ml. and aliquots taken for colorimetric comparison. In determinations 6, 7 and 8 the Na_3AlF_6 was filtered off before comparison, while in 9, 10 and 11 the comparison was made without prior filtration.

This shows that gallium can be determined in the presence of zinc if the ratio of zinc to gallium does not exceed 25,000 to 1, providing the solution contains 0.5 g. of sodium fluoride per liter. If the Na_3AlF_6 was not filtered off, as in determinations 9, 10 and 11, a color was produced if approximately the maximum amounts of both zinc and aluminum, which would give no color when alone, were present, but not when half that quantity of each element was present.

The Determination of Gallium in the Presence of Iron and Aluminum

It was not possible to precipitate the aluminum with sodium fluoride, after the separation of iron with an excess of sodium or potassium hydroxide, due to the interference of the large amount of alkali salts introduced. This made it necessary to acidify the solution after the removal of iron and precipitate the hydroxides of gallium and aluminum by ammonium hydroxide. If this precipitate was filtered on the best grade of filter paper it was found that traces of iron were extracted from the paper during the boiling with hydrochloric acid necessary to redissolve the hydroxides. To avoid this interference the solution was filtered through a Gooch crucible containing a mat of purified anthracene or phenanthrene.[10,11]

Procedure.—The iron was separated as described under "The Determination of Gallium in the Presence of Iron and Indium" and the filtrate acidified with hydrochloric acid. The aluminum and gallium hydroxides were precipitated with ammonium hydroxide according to Blum's method[12] and filtered through a Gooch crucible containing an anthracene or phenanthrene mat, supported on a perforated disk. The precipitate and mat were transferred to the original beaker and boiled with hydrochloric acid. The filtering medium was filtered off through a paper previously washed with 5 *N* hydrochloric acid. The aluminum was then separated by means of sodium fluoride and the gallium determination completed in the usual manner. If only a half milligram of aluminum or less was present, the gallium was determined directly without any separation from that element. The results are shown in Table V.

TABLE V

SEPARATION OF GALLIUM FROM ALUMINUM AND IRON

No.	Al, mg.	Fe, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	10.0	1.0	0.000	0.000	±0.000
2	10.0	1.0	.005	.006	+ .001
3	10.0	1.0	.020	.020	± .000
4	10.0	1.0	.050	.045	− .005
5	15.0	1.0	.010	.008	− .002
6	1.0	1.0	.010	.008	− .002
7	0.5	1.0	.000	.000	± .000
8	.5	1.0	.005	.0055	+ .0005
9	.5	1.0	.010	.008	− .002
10	.5	1.0	.050	.045	− .005
11	.5	1.0	.030	.030	± .000

In Nos. 1–6, the Na_3AlF_6 was filtered off. In Nos. 7–11 no separation of the aluminum was made. Nos. 3, 4, 5, 6, 9, 10 and 11 were diluted to 100 ml. and aliquots taken for comparison.

It is therefore possible to determine gallium in the presence of iron and aluminum when both of the latter are present in as large an amount as is permissible when either is present alone.

The Determination of Gallium in the Presence of Lead, Copper, Tin, Antimony, Germanium and Platinum

Procedure.—The strongly hydrochloric acid solution containing the above elements was distilled to remove germanium. The acidity of the remaining solution was adjusted so as just to prevent precipitation by hydrolysis, and stirred with a small excess of cadmium metal (40 to 60 mesh). The precipitated metals and excess of cadmium were filtered off, 2 to 3 ml. of concd. sulfuric acid added to the filtrate and evaporated to fumes to expel hydrochloric acid. Approximately 100 ml. of water was added and the cadmium removed by electrolysis. This was followed by treatment with hydrogen sulfide to remove the last traces of cadmium and any of the other metals which might be remaining. After filtration and washing, the filtrate was reduced in volume by evaporation, treated with an excess of sodium hydroxide, potassium permanganate, etc., and the determination completed as previously given.

By this method 0.01 mg. of gallium could be determined in the presence of 0.1 g. of each of the above metals either singly or as a mixture.

TABLE VI

THE DETERMINATION OF GALLIUM IN THE PRESENCE OF LEAD, COPPER, TIN, ANTIMONY, GERMANIUM AND PLATINUM

No.	Milligrams		Ga taken, mg.	Ga found, mg.	Error, mg.
1	Pb 100		0.000	0.000	±0.000
2	Pb 100		.010	.012	+ .002
3	Pb 100		.100	.090	− .010
4	Cu 100		.000	.000	± .000
5	Cu 100		.010	.010	± .000
6	Cu 100		.050	.050	± .000
7	Sn 100		.000	.000	± .000
8	Sn 100		.010	.012	+ .002
9	Sn 100		.050	.053	+ .003
10		Sb 100	.000	.000	± .000
11		Sb 100	.010	.011	+ .001
12		Sb 100	.050	.045	− .005
13	Sn 100	Sb 100	.000	.000	± .000
14	Sn 100	Sb 100	.010	.010	± .000
15	Sn 100	Sb 100	.050	.048	− .002
16	Pb 100	Cu 100	.000	.000	± .000
17	Pb 100	Cu 100	.010	.008	− .002
18	Pb 100	Cu 100	.100	.105	+ .005
19	Ge 30		.000	.000	± .000
20	Ge 30		.010	.008	− .002
21	Ge 30		.100	.107	+ .007
22	Ge 30		.000	.000	± .000
23	Ge 30		.010	.011	+ .001
24	Ge 30		.050	.050	± .000
25	Pt 20		.000	.000	± .000
26	Pt 20		.010	.012	+ .002
27	Pt 20		.050	.053	+ .003

In numbers 22, 23 and 24 the germanium was separated by precipitation as the sulfide.

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(10) Gooch, *Proc. Am. Acad. Arts Sci., New Series*, **12**, 390 (1884–85).

(11) These latter substances were purified by dissolving in hot acetone and pouring slowly with constant agitation into an equal volume of concentrated hydrochloric acid. The precipitated anthracene or phenanthrene was filtered off and washed first with hot dilute hydrochloric acid and then with hot water. It was then crystallized from acetone or toluene. If this product, when boiled with hydrochloric acid, gave an extract which produced a color with quinalizarin under the conditions of the colorimetric determination, the process was repeated.

(12) Blum, THIS JOURNAL, **38**, 1282 (1916).

A direct precipitation of more than a trace of the sulfide metals with hydrogen sulfide from a 0.3 *N* acid solution usually resulted in loss of gallium due to its being carried down with the sulfide precipitate, except with the small amount of germanium which was present. In this case, a quantitative separation was obtained by precipitating this element with hydrogen sulfide from 6 to 8 *N* hydrochloric acid. Results obtained are shown in Table VI.

General Procedure.—Obtain the substance in a hydrochloric acid solution and filter off any silver, lead and mercurous mercury which may have precipitated as chloride. Follow this by the procedure given under "The determination of Gallium in the presence of Lead, Copper, Tin, Antimony, Germanium and Platinum." Next separate iron, indium and aluminum, and determine gallium according to the procedure given under "The determination of Gallium in the presence of Iron and Aluminum." This will remove all interfering elements except vanadium and molybdenum, for which no satisfactory separation was found. As much as 100 mg. of lead, copper, antimony, tin, zinc, indium and doubtless that much platinum and germanium may be present, but more than 10 mg. of aluminum and one milligram of iron cause difficulty.

Summary

1. A method for the colorimetric determination of gallium has been developed, based upon the formation of a pink to amethyst colored lake with quinalizarin. The optimum condition is a solution which is normal in ammonium acetate, 0.5 *N* in ammonium chloride, of *p*H 5.0 and containing 0.5 g. of sodium fluoride per liter. Under these conditions 0.02 mg. of gallium per liter can be distinguished. The best concentrations for comparison, using 50-ml. Nessler tubes, lie between 0.02 and 0.2 mg. of gallium per liter.

2. Methods have been developed for separating minute amounts of gallium from 100 mg. of those metals which interfere by giving colored lakes under the same conditions, namely, lead, copper, tin, antimony, indium, platinum and germanium, except that not more than 10 mg. of aluminum, nor 1 mg. of iron should be present, while vanadium and molybdenum must be absent.

ANN ARBOR, MICH. RECEIVED SEPTEMBER 24, 1936

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The Hydration of Unsaturated Compounds. IV. The Rate of Hydration of Isobutene in the Presence of Silver Ion. The Nature of the Isobutene–Silver Complex[1]

BY W. F. EBERZ, H. J. WELGE, DON M. YOST AND H. J. LUCAS

It has been shown that certain soluble metallic salts, such as those of copper, nickel, manganese, etc., have little or no effect upon the rate with which dilute nitric acid catalyzes the hydration of isobutene,[2] whereas in the presence of mercuric nitrate only the isobutene which is not combined with the mercury undergoes hydration. A similar study of the hydration of isobutene in the presence of silver ion is of interest, not only from the theoretical but also from the practical point of view, since silver salts are often added to acids in order to aid the absorption of olefins.

In order to interpret the experimental data obtained from the hydration of isobutene in the presence of silver ion, it is necessary to know the nature of the silver–isobutene complex and the value of the hydration constant of isobutene in the absence of silver ion. The latter is already known.[2]

Nature of the Silver–Isobutene Complex.—This was determined by measuring the distribution ratio of isobutene between, first, carbon tetrachloride and aqueous potassium nitrate, and, second, between carbon tetrachloride and aqueous silver nitrate. In these measurements the ionic strength was maintained constant at 1 *N* by adjusting the concentration of potassium nitrate. In addition to these data, the distribution ratios of isobutene between carbon tetrachloride and pure water, and between carbon tetrachloride and 2 *N* potassium nitrate were also determined. The experimental results are shown in Tables I and II. All concentrations are expressed in moles per liter of solution.

In developing the expressions for the formation of the complex between butene and silver ion,

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(1) For the previous publication in this series, see Lucas and Liu, THIS JOURNAL, **56**, 2138 (1934).

(2) Lucas and Eberz, *ibid.*, **56**, 460 (1934).

TABLE I

DISTRIBUTION RATIO, $(B)_c/(B)$, OF ISOBUTENE BETWEEN CCl_4 AND H_2O AT 25°

Molal concn. of C_4H_8 in CCl_4 $(B)_c$	H_2O (B)	K_D
1.234	0.002055	602
0.989	.001623	609
.782	.001268	616
.4845	.000802	604
.428	.000702	609
.378	.000632	598
.3378	.0005565	606
		Mean 606
CCl_4 and 1 N KNO_3 at 25°		
1.0775	0.001287	838
0.667	.000812	822
		Mean 830
CCl_4 and 2 N KNO_3 at 25°		
0.910	0.000850	1070
.666	.000611	1090
		Mean 1080

TABLE II

DISTRIBUTION OF ISOBUTENE BETWEEN CCl_4 AND $AgNO_3$ + KNO_3 AQ. AT 1μ, AND THE EQUILIBRIUM CONSTANT, K_C, FOR THE ISOBUTENE–SILVER COMPLEX

$AgNO_3$ (Agt) m	Molal concn. of C_4H_8 in CCl_4 $(B)_c$	H_2O (Bt)	K_C
1.000	0.1460	0.01096	62.0
0.978	.06898	.005176	63.0
.965	.06938	.005176	63.5
.7477	.1492	.00845	62.2
.4948	.15415	.00560	59.6
.2484	.1555	.00294	59.8
			Mean 61.7

and for the hydration rate in silver nitrate solution, the following notation is used:

(Bt) = Total isobutene concentration, moles per liter, at time t
(B) = Free isobutene concentration, moles per liter, at time t
(BAg) = Complexed isobutene concentration, moles per liter, at time t
$(Ag)^+$ = Free silver concentration, moles per liter, at time t
(Agt) = Total silver concentration, moles per liter, at any time
$(B)_c$ = Butene concentration, moles per liter, in carbon tetrachloride
K_D = Distribution constant of isobutene between carbon tetrachloride and 1 N potassium nitrate = 830
K_C = Equilibrium constant for the formation of the isobutene–silver complex
$-S$ = The observed specific rate of disappearance of isobutene
k' = The reaction rate constant for the hydration of free butene under the conditions of the run under consideration
k'' = Same, of the complexed butene
k'_e = The expected rate constant for free butene, under the same conditions

$$K_D = (B)_c/(B) \qquad (1)$$

$$K_C = (BAg)/(B)(Ag^+) \qquad (2)$$

Equation (2) is true if the complex is made up of one mole of isobutene and one of silver ion.

Combining (1) and (2)

$$K_C = K_D(BAg)/(B)_c(Ag^+) \qquad (3)$$

and, by the proper substitutions, it is possible to obtain K_C in terms of quantities which can be determined experimentally, that is

$$K_C = K_D[(Bt) - (B)_c/K_D]/(B)_c[(Agt) - (Bt) + (B)_c/K_D] \qquad (4)$$

The values of K_C calculated by the use of equation (4), are shown in Table II. There seems to be a slight trend in these values, for they are smallest at the lowest silver concentrations. But since K_C is quite sensitive to variations in (Bt), especially when the latter has a small value, the trend is probably less significant than it appears to be. The fact that K_C is fairly constant over a four-fold change in the silver ion concentration shows that the correct ratio of butene to silver in the complex is 1:1. This ratio raises the question of the nature of the bond or bonds between the silver ion and the isobutene molecule, for generally the coördination number of silver is two. In order to gain a better understanding of compounds of this type, complexes of silver ion with other olefins, and complexes of isobutene with other metallic ions are being investigated.

Hydration in the Presence of Silver Ion.—The amount of isobutene hydrated in unit time at a given total butene concentration is very much decreased on the addition of silver nitrate, but the amount which actually hydrates exceeds that expected from the calculated free butene concentration. Because this relationship holds in the five experiments where the silver nitrate concentration is substantial (0.24 to 0.74 N), it was thought at first that possibly the complexed, as well as the free, butene hydrates. On this assumption reaction rate constants were calculated for the hydration of the complex. These were found not to be constant, but to vary substantially inversely as the concentration of silver ion. This led to the conclusion that only the free butene hydrates.

The following relations between observed and derived quantities were used. The expressions developed are rigorous, as no simplifying assumptions were made in deriving them. The concentration of silver ion, which can also be obtained from a second, somewhat complicated, expression, results more simply by using the concentration of free butene. For that reason, the derivation of the expression for the butene concentration (equation 12) is given.

Expressions for (B) and (Ag$^+$), the Concentrations of Free Butene and of Silver Ion.—

$$(\mathrm{Ag}t) = (\mathrm{Ag}^+) + (\mathrm{BAg}) \tag{5}$$

$$(\mathrm{B}t) = (\mathrm{B}) + (\mathrm{BAg}) \tag{6}$$

Combining (5) and (6)

$$(\mathrm{Ag}^+) = (\mathrm{Ag}t) - (\mathrm{B}t) + (\mathrm{B}) \tag{7}$$

From (2), (6) and (7)

$$K_\mathrm{C} = \frac{(\mathrm{B}t) - (\mathrm{B})}{(\mathrm{B})[(\mathrm{Ag}t) - (\mathrm{B}t) + (\mathrm{B})]} \tag{8}$$

$$K_\mathrm{C}(\mathrm{B})(\mathrm{Ag}t) - K_\mathrm{C}(\mathrm{B})(\mathrm{B}t) + K_\mathrm{C}(\mathrm{B})^2 = (\mathrm{B}t) - (\mathrm{B}) \tag{9}$$

$$K_\mathrm{C}(\mathrm{B})^2 - (\mathrm{B})[K_\mathrm{C}(\mathrm{B}t) - K_\mathrm{C}(\mathrm{Ag}t) + 1] - (\mathrm{B}t) = 0 \tag{10}$$

Let

$$K_\mathrm{C}(\mathrm{B}t) - K_\mathrm{C}(\mathrm{Ag}t) + 1 = \mathrm{U} \tag{11}$$

then

$$(\mathrm{B}) = \frac{\mathrm{U} \pm \sqrt{\mathrm{U}^2 + 4K_\mathrm{C}(\mathrm{B}t)}}{2K_\mathrm{C}} \tag{12}$$

Derivation of the Rate Expression.—Assuming that only the free butene hydrates, the rate of disappearance is given by equation (13)

$$-\,\mathrm{d}(\mathrm{B}t)/\mathrm{d}t = k'(\mathrm{B}) \tag{13}$$

Combining (2) and (6)

$$(\mathrm{B}) = (\mathrm{B}t)/1 + K_\mathrm{C}(\mathrm{Ag}^+) \tag{14}$$

Combining (13) and (14)

$$-\frac{\mathrm{d}(\mathrm{B}t)}{\mathrm{d}t} = \frac{k'(\mathrm{B}t)}{1 + K_\mathrm{C}(\mathrm{Ag}^+)} \tag{15}$$

$$-S = -\frac{\mathrm{d}\ln(\mathrm{B}t)}{\mathrm{d}t} = \frac{k'}{1 + \mathrm{K_C}(\mathrm{Ag}^+)} \tag{16}$$

That is, the slope of the plot of ln (Bt) against t, which is the observed specific rate of disappearance of isobutene in silver nitrate solution, is related to k', the rate constant of hydration of free isobutene; equations 16, 12 and 7 permit the calculation of k'.

In case the complexed butene also is assumed to hydrate, the rate expression is

$$-\,\mathrm{d}(\mathrm{B}t)/\mathrm{d}t = k'_e(\mathrm{B}) + k''(\mathrm{BAg}) \tag{17}$$

and it may be shown that

$$k'' = -\frac{S\{1 + K_\mathrm{C}[(\mathrm{Ag}t) - (\mathrm{B}t) + (\mathrm{B})]\} - k'_e}{K_\mathrm{C}[(\mathrm{Ag}t) - (\mathrm{B}t) + (\mathrm{B})]} \tag{18}$$

Materials and Analytical Methods.—The isobutene was prepared in the manner previously described;[2] the carbon tetrachloride was purified with dichromate and sulfuric acid,[3] and the other chemicals used were of C. P. grade. Silver ion was precipitated by the addition of potassium bromide before adding the standard bromate solution. The precipitate of silver bromide did not interfere with the analytical procedure previously described.[2]

Distribution Measurements.—In a 2-liter flask provided with a mechanical stirrer was placed about 150 ml. of carbon tetrachloride; isobutene was passed through until a sufficient amount was dissolved. In those measurements involving aqueous solutions not containing silver nitrate, the flask was nearly filled with the aqueous phase and the two phase system, immersed in a thermostat at 25.00 ± 0.03°, was agitated for one and one-half hours. After standing for two hours the drops of carbon tetrachloride clinging to the surface were shaken down and samples of each phase were removed under pressure, using a pipet with three-way stopcock, as previously described.[2] The sample of the aqueous phase measured 100 ml., and of the carbon tetrachloride phase, either 3.149 ml. or 10.40 ml. When the aqueous phase contained silver nitrate, a smaller flask containing a smaller volume of the aqueous phase was used, and a smaller sample of this was taken for analysis.

Reaction Rate Measurements.—The solutions were prepared by nearly saturating an aqueous solution of silver nitrate and potassium nitrate with isobutene, and then adding the desired amount of standardized nitric acid to yield the final solution of known concentration of silver nitrate, nitric acid and potassium nitrate. The ionic strength was kept at 1 *N*. The rate measurements were carried out at 25° in the apparatus and according to the procedure previously described. The experimental data and calculated constants are shown in Table III. Two sets of data and constants are given for each run, *viz.*, a set of initial values and a set of subsequent values. These last are either the final ones for the run, or else, in case the final slope is not the best one, intermediate values. In all cases there is a marked decrease in butene concentration between the initial and later values.

The Rate Constants.—In Table III, in the eighth column under $-S$, are given the values of the observed rate constants. These were obtained by multiplying by 2.303 the slopes of the curves of runs 1 to 5 inclusive in Fig. 1; these are the plots of $\log_{10}(\mathrm{B}t) + 2$ against the time in hours. In the ninth column under k', are the

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(3) Griffin, "Technical Methods of Analyses," McGraw-Hill Book Co., Inc., New York, 1921, p. 77.

TABLE III

RESULTS OF THE HYDRATION EXPERIMENTS, AND THE HYDRATION CONSTANTS

Expt.	HNO_3 m	KNO_3 m	$AgNO_3$ m (Ag*t*)	C_4H_8 m (B*t*)	(B) m calcd.	(Ag^+) m calcd.	$-S$ hrs.$^{-1}$	k' hrs.$^{-1}$	k_e' hrs.$^{-1}$	k'' hrs.$^{-1}$
1	0.2427	0.50	0.2431	0.04259	0.00314	0.2036	0.0472	0.634	0.5005	0.0111
1	.2427	.50	.2431	.01302	.00085	.2301	.0425	.649	.5005	.0104
2	.2428	.375	.3639	.06162	.00310	.3054	.0335	.664	.4994	.00877
2	.2428	.375	.3639	.02943	.00135	.3359	.03065	.667	.4994	.00803
3	.2427	.25	.490	.08503	.00325	.408	.02435	.637	.4996	.00549
3	.2427	.25	.490	.03500	.00120	.456	.02215	.646	.4996	.00519
4	.2433	.125	.6157	.1268	.00404	.4929	.02045	.655	.5011	.00465
4	.2433	.125	.6157	.0320	.00086	.5846	.01845	.685	.5011	.00507
5	.2417	.00	.7346	.1551	.00419	.5836	.01733	.641	.4954	.00406
5	.2417	.00	.7346	.0504	.00116	.6854	.01480	.641	.4954	.00344
6	.100	.0125	.0125	.00933	.00596	.0091	.0853	.133	.140	
6	.100	.0125	.0125	.00544	.00332	.0104	.0853	.139	.140	

values of the reaction rate constant calculated by means of equation (16), and in the tenth column, under k_e', the values of the reaction rate constant which would be expected from the known rate of hydration of isobutene[2] in the absence of silver ion, at the same acidity and ionic strength. It is assumed, in calculating k_e', that silver ion and potassium ion are equivalent in regard to ionic strength.

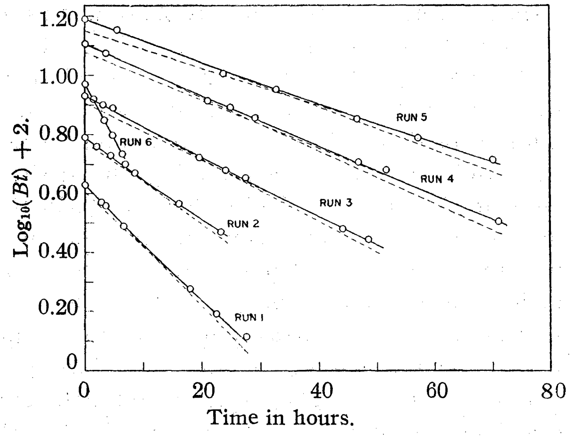

Fig. 1.

The fair constancy of k' at constant acidity and practically constant ionic strength (expts. 1 to 5), over a five-fold change in (B) and a three-fold change in (Ag^+), shows that the rate is first order with respect to uncomplexed butene. Because of the errors involved in taking slopes, the variations in k' are not significant. However, the average value of k', in experiments 1 to 5, is 0.652, whereas 0.499 is the average value of k_e'. Inspection of equation (16) shows that when (Ag^+) becomes zero, k' should be the rate constant in the absence of silver nitrate.

Equation (16) accounts for the observation that $-S$ is substantially inversely proportional to the silver concentration when (Ag*t*) exceeds (B*t*) by a factor of five or more. Also, in any given experiment, $-S$ gradually decreases because (Ag^+) is slowly increasing as the butene undergoes hydration.

The discrepancy between k' and k_e' (expts. 1 to 5) is not due to the hydration of the butene complex since the values of k'', eleventh column, Table III are not constant, but bear an inverse relationship to the concentration of silver ion. In calculating k'' by the use of equation (18), the value of k_e' shown in Table III were used. The discrepancy might be due to an error in K_C. In order for k' to agree with k_e', K_C would have to be smaller by about 25%. This is possible, for there is a slight trend in the values of K_C (Table II). They decrease slightly with a decrease in the ratio of (Ag*t*) to (B*t*). Since this ratio lies between 85 and 188 in the distribution experiments, and between 4.7 and 19 in the rate experiments 1 to 5, the trend in the values of K_C, if there is a trend, would tend to decrease the values of k'. This might account for the discrepancy between k' and k_e' when (Ag*t*)/(B*t*) is large, especially since, in experiment 6, where this ratio lies between 1.2 and 2.3, there is good agreement between k' and k_e'.

Summary

Isobutene and silver ion in aqueous solution form a complex ion for which the formula $C_4H_8Ag^+$ and the equilibrium constant $(C_4H_8Ag^+)/(C_4H_8)(Ag^+) = 61.7$, were determined by distribution measurements.

In 0.25 *N* nitric acid containing silver nitrate the amount of isobutene which hydrates in unit time, at a given concentration of total butene,

is much less than in the absence of silver nitrate, but is greater than corresponds to the amount of free butene. However, satisfactory rate constants were found when it was assumed that only the free butene present in the silver nitrate solution hydrates. The average value of the constants is greater than the known constant in the absence of silver ion. It is concluded that complexed butene does not hydrate.

PASADENA, CALIF. RECEIVED SEPTEMBER 30, 1936

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Analysis of Gamma-Fructoside Mixtures by Means of Invertase. V. Methylated and Acetylated Derivatives of Crystalline α-Methyl- and α-Benzylfructofuranoside[1]

BY C. B. PURVES AND C. S. HUDSON

The products obtained by the action of chemical reagents on fructose are in most instances complex mixtures not easily separable into their constituents by crystallization or by other methods. This circumstance adds greatly to the experimental difficulty of studying the chemistry of the ketose and in consequence also adds to the value of the few crystalline derivatives which have been prepared from it. The very readily hydrolyzed or gamma-methylfructoside isolated two years ago[2b] was a pure crystalline individual[3] and therefore provided a welcome new starting material for such studies, some of which are recorded in this article.

When the highly dextrorotatory tetramethyl derivative of the glycoside was hydrolyzed with aqueous acid, the less dextrorotatory liquid product was found to be tetramethyl fructofuranose.[4] These facts proved that the "crystalline gamma-methylfructoside" or the "glycoside c" of earlier articles[2b,5a,5b] was in reality α-methylfructofuranoside. The methylation of this substance was not easy. Silver oxide and methyl iodide with anhydrous dioxane as an initial solvent yielded fully methylated products with low and variable specific rotations in water (112, 118°) even after the removal of the methylated methyl esters which they contained (up to 17.6%). Dipotassium and tetrapotassium derivatives reacted very slowly and incompletely with methyl iodide even in the absence of liquid ammonia.[6] The satisfactory methylations, carried out with the help of thallous ethylate by a special method adapted from the work of Menzies,[7] gave tetramethyl α-methylfructofuranoside as a mobile liquid free from esters and with a specific rotation of 129.4° in water. An interesting liquid dimethylfructose, whose optical rotation passed through a minimum near 10° and whose methoxyl groups perhaps occupied the 3,4 positions, was prepared from the corresponding dimethyl α-methylfuranoside. The latter was an intermediate product in the thallous ethylate methylations.

A brief search for derivatives of the glycoside which might be of use in its separation from mixtures resulted in the discovery of tetraacetyl α-methylfructofuranoside in the form of crystals melting at 48–48.5° and having a specific dextrorotation of 88.1° in chloroform. The first crystals were obtained after long delay by acetylating the carefully purified glycoside with Liebermann's reagents but were subsequently prepared from sucrose. The fructofuranoside failed to form a sparingly soluble derivative with barium hydroxide or methylate and yielded no crystalline addition compound with alcoholic potassium acetate.[8] When equimolecular amounts of α-methylfructofuranoside and of hydrogen chloride were mixed in concentrated anhydrous dioxane solution, however, a white, gelatinous carbohydrate–hydrogen chloride addition compound immediately separated and at once began to decompose to a dark, copper reducing tar. Although this ill-defined and highly unstable complex was of a type new to sugar chemistry, such compounds have been inferred to exist as transitory inter-

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] Purves and Hudson, (a) THIS JOURNAL, **56**, 702 (1934); (b) **56**, 708 (1934).

[3] Melting at 80.5–81° and not at 69° as previously stated.

[4] Haworth, Hirst and Nicolson, *J. Chem. Soc.*, 1513 (1927).

[5] Purves, THIS JOURNAL, (a) **56**, 1969 (1934); (b) **56**, 1973 (1934).

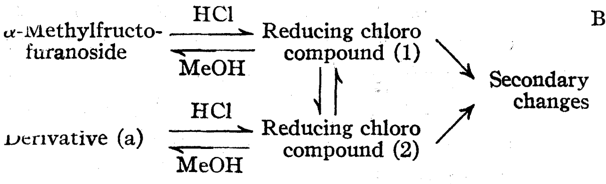
[6] Muskat, *ibid.*, **56**, 2449 (1934).

[7] Fear and Menzies, *J. Chem. Soc.*, 937 (1926).

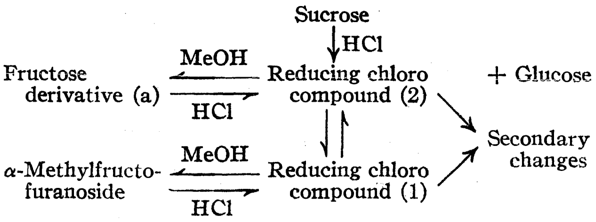
[8] *Cf.* Watters, Hockett and Hudson, THIS JOURNAL, **56**, 2199 (1934).

mediates in the transformations of glycosides dissolved in acid alcohols. Voss and Wachs[9] recently studied some aspects of the subject and discussed the relevant literature.

In the present case, no precipitate appeared when the dioxane solution was 0.0263 molar with respect to the glycoside and 0.025 normal with hydrogen chloride. The change with time both in the specific rotation (Fig. 1 Curve A) and in the copper reducing power of the solution (Fig. 1 Curve B) pointed to the occurrence of a complicated sequence of reactions. The maximum reduction attained, 49% of that theoretically possible, suggested that about half of the hydrogen chloride existed at this point as a copper-reducing chloro addition or substitution compound. After twenty-two hours at 20° almost half of the carbohydrate had been destroyed. The entire data supported the conclusion that a very rapid addition of hydrogen chloride to the fructofuranoside was followed by the formation of a highly unstable, copper reducing chloro compound. This partly decomposed and partly recombined with hydroxyl groups in the fructose molecule, thereby liberating hydrogen chloride which united with more of the glycosidic residues. These ideas supply an attractive explanation of the behavior of α-methylfructofuranoside in methyl alcoholic hydrogen chloride, when the starting material very rapidly attained an equilibrium with a second non-reducing gamma-fructose derivative (a) which was hydrolyzed by invertase[5a]

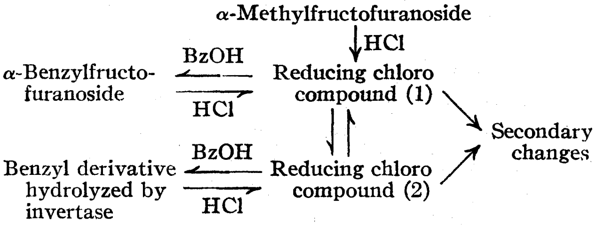


In this reaction the reduction was negligible throughout and the secondary changes were inappreciable for several hours. The concentration of intermediate chloro compounds was apparently restricted to a minute figure by an extremely rapid recombination with the large excess of methyl alcohol present. As shown in the scheme, this partial transformation of the glycoside suggested the nature of the primary equilibrium supposed to exist between the chloro compounds (1) and (2). Another example was drawn from the research already published[5b] concerning the scission of sucrose in methyl alcohol containing hydrogen chloride. The experimental data were consistent with the following set of reactions



A distinct optical exaltation was displayed by the sucrose–acid methyl alcoholic solution during the first few minutes. This was due possibly to the formation of a sucrose–hydrogen chloride addition compound.

If the above views on the mechanism of the interaction between α-methylfructofuranoside and methyl alcohol containing hydrogen chloride were correct, it was possible to use the fructoside in synthetical operations by substituting another hydroxylic compound for the methyl alcohol. Benzyl alcohol was chosen because it was expected to give crystalline derivatives of convenient solubility from which it might eventually be removed quantitatively, as toluene, by hydrogenation with palladium.[10] The following reactions were predicted in acid benzyl alcohol



The specific rotation of α-methylfructofuranoside in the new, acid solvent first decreased very rapidly and then much more slowly (Fig. 1, Curve C), the break in the curve (region C) signalizing the end of the primary change. The product isolated at this time included reducing substances (8 mol. % as fructose) and a new, non-reducing benzyl derivative (28 mol. %) which had a calculated specific levorotation of −27° in water and was hydrolyzed to fructose by the enzyme invertase. These two constituents were removed by a fermentation with yeast and α-benzylfructofuranoside (26.5 mol. %) was recovered as a crystalline tetraacetate from the unfermented portion of the product. By the end of the primary reaction, therefore, the origi-

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(9) Voss and Wachs, *Ann.*, **522**, 240 (1936).

(10) Richtmyer, This Journal, **56**, 1633 (1934).

nal gamma-methylglycoside had been largely replaced by a mixture of gamma-benzylglycosides.

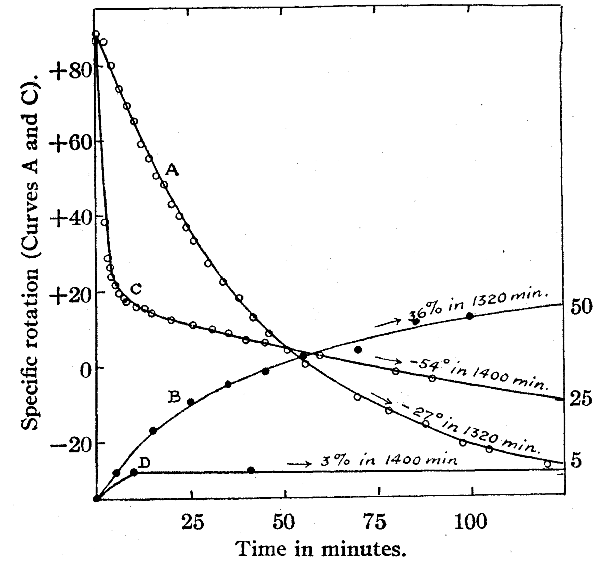

Fig. 1.—Action of hydrogen chloride on α-methylfructofuranoside: (A), specific rotation in dioxane; (B), copper reduction in dioxane; (C), specific rotation in benzyl alcohol; (D), copper reduction in benzyl alcohol.

The facts that the secondary optical change was fairly rapid and that a maximum copper reduction of 8 mol. % developed in the solution (Fig. 1, Curve D) suggested that labile chloro compounds accumulated as such in considerable amount and had time to undergo secondary transformations prior to recombination with the solvent.

Tetraacetyl α-benzylfructofuranoside was a beautifully crystalline substance melting at 84.5–85° and with a specific dextrorotation of 64.7° in chloroform. Deacetylation yielded α-benzylfructofuranoside as stout, rectangular tablets with a melting point of 89° and specific dextrorotations of 45.7 and 47.6° in water and dioxane, respectively. The new glycoside was hydrolyzed to fructose by aqueous acid 16.5 times more rapidly than sucrose but was unaffected by invertase or by yeast fermentation. When methylated with thallous ethylate it gave first a liquid dimethyl derivative and finally liquid tetramethyl α-benzylfructofuranoside with dextrorotations of 78.4° in dioxane and of 83.3° in chloroform. Scission of the latter with methyl alcoholic followed by aqueous hydrogen chloride resulted in an 80% yield of tetramethyl fructofuranose.[4] The isolation of the latter established the constitutions assigned to this series of benzyl derivatives.

The behavior of pure α-benzylfructofuranoside in benzyl alcoholic hydrogen chloride was similar to that of its methyl homolog in the same solvent. A very rapid primary decrease in specific rotation was followed by a fairly rapid secondary change (Fig. 2, Curve A) and was accompanied by the development of a substantial copper reduction (not plotted). The product isolated by arresting the reaction in the region A was submitted to the action of a powerful solution of invertase, which caused the copper reducing power of the mixture to increase from 12.4 mol. % to a final constant value of 44.8 mol. % as fructose. In Fig. 2, Curve C, the increase in the reduction at each time was plotted as a percentage of the total *enzymotic* increase, and from the curve the rate of hydrolysis was found to be about 5.1 times slower at each stage than the rate observed in an equivalent inversion of sucrose. A small initial exaltation in the optical rotatory power (Fig. 2, Curve B) paralleled the similar observation made during the partial hydrolysis of a gamma-methylfructoside mixture with invertase.[2a] The polarimetric and copper-reduction data enabled a specific levorotation of −27 ± 2° in water to be assigned to the non-reducing benzyl derivative unstable to the enzyme and the stable glycoside, with a dextrorotation of 41°, was mostly α-benzylfructofuranoside. The substrate hydrolyzed by

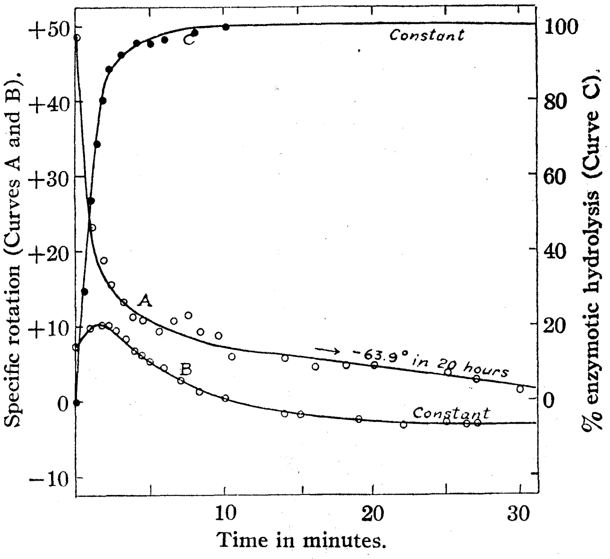

Fig. 2.—(A), Specific rotation of α-benzylfructofuranoside in acid benzyl alcohol; (B), hydrolysis of a gamma-benzyl fructoside mixture with invertase, specific rotation; (C), hydrolysis of the same gamma-benzy fructoside mixture with invertase, copper reduction, %.

invertase consisted of the benzyl and fructoside radicals because these alone were present during its preparation and the calculation assumed it to be a true benzylfructoside of molecular weight 270.

Experimental

Sodium light and a saccharimeter with a conversion factor of 0.3462° circular = 1° V. were used in the optical observations, which were made at 20° in a 2-dm. tube unless otherwise stated. Copper reducing power was expressed throughout as fructose. Previous articles[2,5] stressed the necessity of employing redistilled, anhydrous, acid-free solvents and of avoiding elevated temperatures whenever possible in the preparative work. They also described the method adopted in making up solutions containing hydrogen chloride and gave details of the analytical technique.

Preparation of a Liquid Dimethyl α-Methylfructofuranoside.—Fifteen grams of the pure, recrystallized α-methylfructofuranoside, dissolved in 50 ml. of 100% ethyl alcohol, were shaken vigorously for a few seconds with 100 ml. of 1.615 *N* ethereal thallous ethylate[11] (2 equivalents). The round-bottomed flask used was then attached to a ground-in reflux condenser through the top of which the solvents were thoroughly removed, finally in high vacuum. Access of atmospheric carbon dioxide was minimized during these operations, and the temperature restricted to that of the room or less. The dithallium derivative remaining in the flask as a pale yellow, friable powder was incorporated with 100 ml. of ether containing 15 ml. of methyl iodide (50% excess) before the mixture was warmed under the reflux condenser for six hours, or until a sample was no longer alkaline to moist litmus paper. Sometimes it was necessary to renew the methyl iodide, and to continue the heating. Four 50-ml. portions of ether extracted the product from the insoluble thallous iodide and when the solvent was removed from the combined extracts, finally at 40° in high vacuum, a nearly quantitative yield of a liquid dimethyl α-methylfructofuranoside remained.

Anal. Calcd. for dimethyl methylfructoside, $C_9H_{18}O_6$: C, 48.7; H, 8.1; OCH_3, 41.9. Found: C, 48.5; H, 8.3; OCH_3, 41.5.

The colorless dimethyl methylglycoside had a refractive index of $n^{20}D$ 1.4632 and the following specific dextrorotations: in chloroform, +94.0° (*C*, 1.565; V., +8.50°); in water, +111.4° (*C*, 1.6; V., +10.30°); in dioxane, +95.3° (*C*, 1.508; V., +8.30°). The aqueous solution was quite clear.

A Liquid Dimethyl Fructose.—A solution containing 3.78 g. of the above dimethyl methylglycoside in 0.1 *N* hydrochloric acid was hydrolyzed completely by fifteen minutes of heating at 100°. The product, 3.6 g., isolated by standard methods, had a refractive index of $n^{19}D$ 1.4768 and a methoxyl content of 29.3% (calcd. for dimethyl fructose, $C_8H_{16}O_6$: OCH_3, 29.8%). A 2.061% aqueous solution had a levorotation of −1.30° V. five minutes after solution, changing to a final constant value of −2.05° V. within two hours. These data corresponded to a mutarotation from $[\alpha]^{20}D$ −10.9° to $[\alpha]^{20}D$ −17.2°. At temperatures of 4, 10, 17, 30 and 45° the same solution displayed specific rotations of −16.8, −18.9, −18.1, −15.5 and −11.3°, respectively. The rotation therefore passed through a minimum in the neighborhood of 10°.

Tetramethyl α-Methylfructofuranoside.—The methylation of the dimethyl α-methyl derivative, 12.63 g., was carried out with 2 equivalents of ethereal thallous ethylate and 2.7 mols of methyl iodide in the way already described. Ether, 100 ml., was used in place of absolute alcohol as the initial solvent. The reaction was not quite complete (found: OCH_3, 58.0%) and a single treatment with silver oxide and methyl iodide was necessary before the product was distilled with high vacuum into a very well cooled receiver. The yield was 11.68 g. with a refractive index of $n^{20}D$ 1.4417 which was identical with that of the last drop.

Anal. Calcd. for tetramethyl methylfructoside, $C_{11}H_{22}O_6$: C, 52.8; H, 8.8; OCH_3, 62.0. Found: C, 52.9; H, 8.9; OCH_3, 61.4.

Tetramethyl α-methylfructofuranoside was a mobile, colorless liquid which gave a clear aqueous solution taking up no alkali and therefore containing no esters. Its specific dextrorotation was: +115.9° in chloroform (*C*, 2.279; V., +15.26°); +113.1° in dioxane (*C*, 2.120; V., +13.85°); and +129.4° in water (C, 2.6; V., +19.45°).

The methylated fructofuranoside, 4.45 g., was hydrolyzed and the tetramethyl fructofuranose produced was isolated and distilled by standard methods; yield 3.88 g. or 92%.

Anal. Calcd. for tetramethylfructose, $C_{10}H_{20}O_6$: C, 50.9; H, 8.5; OCH_3, 52.5. Found: C, 50.9; H, 8.7; OCH_3, 51.9.

Its refractive index, $n^{20}D$ 1.4517, and specific rotation in water, +28.1° initially to +29.8° finally, were in agreement with the accepted constants for this compound ($n^{13}D$ 1.4513; $[\alpha]D$ +31.3°).[4]

Preparation of Tetraacetyl α-Methylfructofuranoside from Sucrose.—A fermented, aqueous solution of α-methylfructofuranoside contaminated with glucofuranosides was prepared from 180 g. of sucrose by the method already published.[5b] A cautious evaporation of the neutralized solution (*p*H 8) without the addition of butyl alcohol left 65 g. of a thick sirup. This was acetylated by shaking at room temperature with 20 g. of anhydrous sodium acetate and 320 ml. of acetic anhydride and by heating the resulting solution for ninety minutes on the steam-bath. The water-soluble product, recovered by standard methods in a total of 600 ml. of neutral, dry benzene, was a thick, orange colored sirup weighing 100 g. Crude, nearly colorless tetraacetyl α-methylfructofuranoside, 92 g., passed into the receiver when this sirup was fractionated in high vacuum; bath 200–230°. A more accurate fractionation than that carried out would probably have rendered the following crystallization less difficult. Two volumes of water were added to one volume of a 20% solution of the distillate in methyl alcohol, the solution was cooled until it was definitely opalescent and the clear supernatant liquid was copiously nucleated in a separate vessel which was kept for three days at 0–5°; yield 35 g., increased to 40 g. by working up and redistilling the mother liquors and residues. A similar but easy re-

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[11] Menzies, *J. Chem. Soc.*, 1571 (1930). Crude, moist thallous hydroxide was first prepared by adding the equivalent of baryta to a hot 15% thallous sulfate solution and by cautiously evaporating the filtrate.

crystallization left 36 g. or 38% of the calculated amount of the product in a pure condition. The sample for the rotations and analyses was dried in a vacuum over soda lime.

Anal. Calcd. for tetraacetyl methylfructoside, $C_{15}H_{22}O_{10}$: C, 49.7; H, 6.1; OCH_3, 8.6. Found: C, 49.5; H, 6.1; OCH_3, 8.6, 8.5.

In an acetyl estimation (Kunz' method)[12] 0.2043 g. required 22.6 ml. of 0.1 *N* alkali; calcd. 22.6 ml. The deacetylation of 2.64 g. by 100 ml. of anhydrous, 0.00068 normal methyl alcoholic barium methylate left 1.38 g. of pure α-methylfructofuranoside, with the correct specific rotation of +91.7° in methyl alcohol; calcd. 1.416 g.

The matted fine needles or large, well-built stout prisms of tetraacetyl α-methylfructofuranoside melted at 48–48.5°, dissolved in water and petroleum ether and were very soluble in the other common organic solvents. The compound had the following specific dextrorotations observed at 19°: +88.1° in chloroform (*C*, 4; V., +20.35°); +84.4° in dioxane (*C*, 4; V., +19.50°); +91.3° in methyl alcohol (*C*, 2.069; V., +10.92°); and +84.0° in water (*C*, 1; V., +9.70° observed in a 4-dm. tube).

The Carbohydrate–Hydrogen Chloride Addition Compound.—A 12.76% solution of α-methylfructofuranoside in warm dioxane was cooled to room temperature before 10 ml. was mixed quickly with 2 ml. of dioxane made 2.63 *N* with hydrogen chloride. The mixture was therefore 0.526 *M* with respect to both constituents. The white gelatinous fluid rapidly darkened in color as a difficult filtration gave a colorless filtrate the first portion of which, 4.7 ml., was diluted immediately to 25 ml. with water and analyzed. Found in the dioxane filtrate: HCl, 0.106 *M* by titration, 0.106 *M* as silver chloride; copper reduction as fructose, 0.038 *M*, increased to 0.052 *M* by a Herzfeld hydrolysis. By difference, the precipitate contained carbohydrate and hydrogen chloride in the molar ratio of 0.474:0.420 or of 1.13:1. The apparent deviation from an exact equimolecular ratio was probably due to the destruction of fructose in the filtrate prior to dilution with water.

Behavior of α-Methylfructofuranoside in Dioxane Containing Hydrogen Chloride.—The solution described in the caption to Table I was prepared and examined by usual methods. After 5, 15, 25, 35, 45, 55, 70, 85, 100, 125, 150, 175, 204 and 1320 minutes its copper reducing power was 6.3, 18.0, 25.4, 30.0, 33.8, 37.4, 39.1, 47.6, 48.6, 50.7, 47.6, 50.7, 47.6 and 36.0%, respectively, of the maximum possible (Fig. 1, Curve B). After 1320 minutes only 52.8% of the original fructose was estimated in a Herzfeld hydrolysis. The polarimetric observations given in Table I were made in a 4-dm. tube.

Action of Anhydrous Benzyl Alcoholic Hydrogen Chloride on α-Methylfructofuranoside.—Samples, 0.5 ml., of the solution described in the caption to Table II were prepared for the estimations of copper reducing power by discharge into 50-ml. volumes of 0.0003 *N* aqueous caustic soda containing 3% of methyl alcohol. After 0, 9.5, 41, 134, 204, 366, 488 and 1400 minutes these reductions were 0.0, 6.9, 7.9, 6.4, 5.9, 4.8, 4.6 and 3.0%, respectively, of the maximum calculated from the fructoside present (see Fig. 1, Curve D). The specific rotations in Table II were calculated as due throughout to methyl glycoside.

TABLE I

OPTICAL ROTATION OF 0.0263 *M* α-METHYLFRUCTOFURANOSIDE IN DIOXANE 0.025 *N* WITH HYDROGEN CHLORIDE AT 18°[a]

Min.	V.° (L = 4)	$[\alpha]^{18}_D$	Min.	V.° (L = 4)	$[\alpha]^{18}_D$
0	+5.24	88.8[b]	38	1.07	18.1
2	5.10	86.4	42	0.77	13.0
4	4.73	80.2	46	.52	8.7
6	4.38	74.2	51	+ .27	+ 4.6
8	4.10	69.5	56	+ .05	+ 0.8
10	3.88	65.8	71	− .51	− 8.6
12	3.50	59.3	78	− .71	−12.0
14	3.28	55.6	88	− .97	−16.4
16	3.01	51.0	98	−1.22	−20.7
18	2.82	47.8	105	−1.31	−22.2
20	2.58	43.7	121	−1.55	−26.3
22	2.37	40.2	145	−1.78	−30.3
24	2.19	37.1	204	−2.10	−35.6
26	2.00	33.9	280	−2.25	−38.1
30	1.63	27.6	1320	−1.6	−27.1[c]
34	1.33	22.5			

[a] See Fig. 1, Curve A. [b] Separately observed in acid-free solvent. [c] Discoloration.

TABLE II

OPTICAL ROTATION OF A 7.8017% SOLUTION OF α-METHYLFRUCTOFURANOSIDE IN 0.03 *N* BENZYL ALCOHOLIC HYDROGEN CHLORIDE AT 20°[a]

Min.	V.°, obsd.	$[\alpha]^{20}_D$	Min.	V.°, obsd.	$[\alpha]^{20}_D$
0	+39.46	+87.6[b]	30	4.45	9.9
2.4	17.25	38.3	35	+ 3.85	+ 8.5
3.2	13.10	29.1	40	+ 3.25	+ 7.2
3.75	11.70	26.0	45	+ 2.70	+ 6.0
4.3	10.70	23.8	60	+ 1.15	+ 2.6
5.25	9.65	21.4	80	− 0.65	− 1.4
6.2	8.75	19.4	90	− 1.50	− 3.3
7.2	8.12	18.0	132	− 4.75	−10.5
8.0	7.75	17.2	180	− 8.25	−17.3
10.5	7.09	15.7	210	−10.05	−22.3
12.5	6.85	15.2	340	−16.85	−37.4
15.0	6.40	14.2	486	−21.10	−46.8
20	5.70	12.7	1140	−24.53	−54.4[c]
25.4	5.00	11.1	1395	−24.10	−53.5

[a] See Fig. 1, Curve C. [b] See Table I, note [b]. [c] $[\alpha]^{20}_D$ −39.1° calcd. as benzyl rather than as methylfructoside.

Preparation of Tetraacetyl α-Benzyl- from α-Methylfructofuranoside.—Ten grams of the finely divided methyl glycoside dissolved almost entirely when vigorously shaken for six minutes at 20° with 100 ml. of benzyl alcohol made 0.03 *N* with hydrogen chloride gas. After six minutes, the acid was neutralized quickly and completely with 2 g. of silver oxide and the pale yellow, silver-free filtrate was diluted with 200 ml. of benzene and 800 ml. of light petroleum. This dilution made it possible to recover 94% of the product from the mixed solvents by three extractions with 100 ml. volumes of water. The combined aqueous extracts were shaken once with ether and prepared for fermentation. Analysis: reduction 0.208%, increased to 0.900% by invertase and to 2.50% by a Herzfeld hydrolysis. Starch-free yeast, 1 g., fermented two components of the mixture and left unfermented 7.92 g. of gamma-benzyl

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[12] Kunz and Hudson, THIS JOURNAL, **48**, 1982 (1926).

fructosides with a specific dextrorotation of 46.2° in water. Cold pyridine, 50 ml., and acetic anhydride, 50 ml., acetylated this sirup overnight. A recrystallization of the product from ether yielded 6.9 g. of sticky crystals with a specific rotation of +64.4° in methyl alcohol. A final recrystallization from 20 ml. of methyl alcohol gave 6.0 g. of pure tetraacetyl α-benzylfructofuranoside, corresponding to 26.5% of the methylfructoside used.

Anal. (Sample dried at 0.1 mm. and 55° for ten hours.) Calcd. for tetraacetyl benzylfructoside, $C_{21}H_{26}O_{10}$: C, 57.5; H, 5.9. Found: C, 57.4; H, 5.9. In an acetyl estimation, 0.2822 g. took 25.9 ml. of 0.1 *N* alkali. Calcd. for four acetyl groups, 25.8 ml.

The glycoside melted sharply at 84.5–85°, was insoluble in water, sparingly soluble in petroleum ether and soluble in other organic solvents. It separated from ether or hot methyl alcohol as stout flat prisms and occasionally as clusters of long needles from a cold dilute solution of the latter solvent. The following specific dextrorotations refer to 4% solutions: in methyl alcohol, +65.65° (V., +15.17°); in chloroform, +64.7° (V., +14.95°) and in dioxane +58.42° (V., +13.50°).

Preparation of α-Benzylfructofuranoside from its Tetraacetate.—Absolute barium methylate, 1.5 ml. of 2 *N*, added to 20 g. of the pure tetraacetate dissolved in 400 ml. of ice-cold, anhydrous methyl alcohol, was just sufficient to render the mixture definitely alkaline to phenol red. After standing overnight at 0°, the faintly yellow solution was evaporated at 0° (30 mm.) to a thick sirup which still contained the trace of unneutralized barium. This was removed by diluting the sirup with 400 ml. of boiling ether and filtering the warm solution through absorbent carbon. The filtrate quickly deposited 9.6 g. of stout, well-built rectangular tablets which adhered to the bottom and sides of the beaker. A further 0.9 g. obtained from the concentrated mother liquor brought the total yield of α-benzylfructofuranoside up to 85% of the theoretical.

Anal. Calcd. for a benzylfructoside, $C_{13}H_{18}O_6$: C, 57.8; H, 6.7. Found: C, 58.0; H, 6.8. A 1.50% solution in 0.25 *N* aqueous acid at 20° had, after complete hydrolysis, a reduction of 0.98% and a levorotation of −5.35°. Calcd. for fructose 1.00% and −5.34° V.

The compound was quite pure when isolated because fractional recrystallizations made by adding ether to a concentrated dioxane solution failed to change the following constants: melting point, 89°; specific dextrorotation in dioxane, +47.60° (*C*, 2; V., +5.50°) and in water, +45.70° (*C*, 2.5; V., +6.60°). α-Benzylfructofuranoside was almost insoluble in petroleum ether, was soluble in benzene and ether and dissolved freely in alcohols, water, and dioxane. Its reduction of the Shaffer–Hartmann alkaline copper reagent was inappreciable. A 1.25% solution of the benzyl gamma-fructoside in 1% aqueous acid sodium phosphate was mixed with a powerful invertase preparation. After twenty hours the mixture still inverted added sucrose rapidly but retained the original rotation and a zero reduction in measurements precise enough to have detected a hydrolysis of 2% with ease. Invertase therefore neither hydrolyzed the glycoside nor was inactivated by it.

Hydrolysis of α-Benzylfructofuranoside by Aqueous Acid.—The changes in the rotation and copper reducing power of a 1.5% solution in 0.25 *N* hydrochloric acid at 20° were followed as described in the case of the α-methyl glycoside.[5a] A unimolecular velocity constant of $10^4K = 72 \pm 1$ (in minutes and decimal logarithms), calculated from reduction data ranging from 8 to 92% hydrolysis, showed the hydrolysis to be 16.5 times more rapid than that determined for sucrose in the equivalent conditions (10^4K for sucrose = 4.3 ± 0.04). The optical observations simultaneously made on the α-benzylfructofuranoside solution corresponded to unimolecular coefficients which rose uniformly from $10^4K = 65.2$ (4.5% Hy.) to $10^4K = 76.8$ (13.8% Hy.). They then diminished steadily to $10^4K = 66.3 \pm 1$ (66.4–95.7% Hy.).

A Liquid Dimethyl α-Benzylfructofuranoside.—Four grams of the pure benzyl glycoside, m. p. 89°, dissolved at room temperature in 25 ml. of 100% ethyl alcohol, gave an immediate, amorphous, pale yellow precipitate of the dithallium derivative when 18.5 ml. of 1.66 *N* ethereal thallous ethylate was added (2 equivalents + 4% excess). The methylation was completed as in the case of the α-methyl glycoside and a nearly theoretical yield of a viscid, dimethyl α-benzylfructofuranoside, $n^{19}\text{D}$ 1.5145, was isolated.

Anal. (Sample heated at 30° in high vacuum.) Calcd. for a dimethyl benzylfructoside, $C_{15}H_{22}O_6$: C, 60.4; H, 7.4; OCH_3, 20.8. Found: C, 60.2; H, 7.6; OCH_3, 21.0.

The substance had a specific dextrorotation of $[\alpha]^{19}\text{D}$ +57.1° in dioxane (*C*, 1.243; V., +2.05°; L = 1).

Tetramethyl α-Benzylfructofuranoside.—The dithallium derivative of the above dimethyl α-benzyl glycoside was prepared as an amorphous white precipitate by adding 2.1 equivalents of ethereal thallous ethylate to 4.1 g. dissolved in 30 ml. of ether. After methylation the product was remethylated with 7 g. of silver oxide and 4 ml. of methyl iodide. Tetramethyl α-benzylfructofuranoside (yield 88%) was a somewhat viscid liquid with a refractive index of $n^{19}\text{D}$ 1.4900 after drying at 35° in a high vacuum.

Anal. Calcd. for tetramethyl benzylfructoside, $C_{17}H_{26}O_6$: C, 62.5; H, 8.0; OCH_3, 38.0. Found: C, 62.5; H, 8.2; OCH_3, 38.2. *Subs.* 0.1215 g. took 0.0 ml. of 0.1 *N* alkali so that esters were absent.

The substance had specific dextrorotations at 19° of +78.4° in dioxane (*C*, 2.134; V., +9.67°), of +83.3° in chloroform (*C*, 2.162; V., +10.40°) and of +78.8° in methyl alcohol (*C*, 1.29; V., +5.87°). It was insoluble in water but dissolved readily in organic solvents.

Hydrolysis of Tetramethyl α-Benzylfructofuranoside.—The benzyl group of the water-insoluble glycoside was first replaced by the methoxyl radical by solution (3.1 g.) in 72 ml. of 0.03 *N* methyl alcoholic hydrogen chloride at 19°. Fifteen hours later, when the specific rotation had diminished to a steady dextro value of 33.7°, calculated as benzyl fructoside, the resultant mixture of water-soluble tetramethyl gamma-methylfructosides and benzyl alcohol was isolated and hydrolyzed by aqueous acid in the usual way. Ether, 50 ml., extracted most of the benzyl alcohol (and 5% of the product) from the neutralized hydrolysate (80 ml.) and chloroform subsequently extracted crude tetramethyl fructofuranose; yield 91.3% after distillation. The product still contained some benzyl alcohol (found, OCH_3, 46.4%; $n^{19}\text{D}$ 1.4585) and was fractionated in high vacuum. The first fraction containing the alcohol was rejected (0.70 g.; n^{20}_D 1.4735) and the second fraction was practically pure tetramethyl fructofuranose (1.23 g. or 49%).

Anal. Calcd. for tetramethyl fructose, $C_{10}H_{20}O_6$: C, 50.9; H, 8.5; OCH_3, 52.5. Found: C, 51.0; H, 8.6; OCH_3, 50.3.

The refractive index and the specific rotation in water, n^{19}_D 1.4508 and $[\alpha]^{20}_D$ +29.8° (final value), respectively, were in good agreement with the constants accepted for tetramethyl fructofuranose (n^{13}_D 1.4513, $[\alpha]_D$ +31.3°).[4]

Behavior of α-Benzylfructofuranoside in Benzyl Alcoholic Hydrogen Chloride.—After 0, 1.3, 2, 2.5, 12.7, and 1560 minutes the copper reducing power of the solution described in the caption to Table III was 0, 4.4, 6.5, 7.8, 22.1 and 5.1%, respectively, of the maximum possible from the fructose glycoside present. These reductions were determined by discharging 0.5-ml. samples into Shaffer–Hartmann boiling tubes each containing 1 ml. of a mixture of purified dioxane (5 parts) and 0.1 *N* aqueous caustic soda (1 part). Water, 3.5 ml., was added to each before the estimation, which was of less than usual accuracy. A 1-dm. polarimeter tube was used in the optical observations.

TABLE III

OPTICAL ROTATION OF A 2.25% SOLUTION OF α-BENZYLFRUCTOFURANOSIDE DISSOLVED IN 0.03 *N* BENZYL ALCOHOLIC HYDROGEN CHLORIDE AT 20°[a]

Min.	V.°, obsd.	$[\alpha]^{20}_D$	Min.	V.°, obsd.	$[\alpha]^{20}_D$
0	+3.15	+48.5[b]	23	0.30	4.6
1	1.51	23.2	25	.23	3.5
1.75	1.22	18.8	27	.18	2.8
2.3	1.09	15.5	30	.08	1.2
3.2	0.87	13.4	35	.00	0.0
3.75	.72	11.1	40	− .10	− 1.5
4.5	.70	10.8	45	− .19	− 2.9
5.5	.60	9.2	55	− .40	− 6.2
6.5	.70	10.8	70	− .65	−10.0
7.5	.75	11.6	90.2	− .92	−14.2
8.3	.60	9.2	113	−1.31	−20.2
9.5	.55	8.5	144	−1.72	−26.5
10.3	.53	8.2	180	−2.22	−33.5
14	.37	5.7	270	−2.93	−44.4
16	.29	4.5	465	−3.87	−59.6
18	.30	4.6	1200	−4.15	−63.9
20	.30	4.6	1500	−4.05	−62.3

[a] See Fig. 2, Curve A. [b] See Table I, note *b*.

Partial Hydrolysis of a Benzyl-furanoside Mixture with Invertase.—A solution consisting of 2.00 g. of α-benzylfructofuranoside dissolved in 25 ml. of anhydrous 0.01 *N* benzyl alcoholic hydrogen chloride was observed at 23° for twelve minutes on the saccharimeter or until its specific dextrorotation had decreased to +9.5° (Fig. 2, Curve A, region A). The acid was neutralized thoroughly with silver oxide after fourteen minutes, and the product recovered in 40 ml. of water containing 4 ml. of 2% sodium hydrogen phosphate.[13] This faintly acid solution (*p*H 4.5) had an observed dextrorotation of +1.98° and a copper reduction of 0.392%, increased to 3.15% by a Herzfeld hydrolysis. These values were unchanged after twenty hours at 23°. An equal volume of powerful invertase solution was then added and the consequent changes in optical rotation observed in a 4-dm. tube (Table IV). The specific rotations were calculated as entirely due to $[(3.15/2) \times (3/2)]$ or 2.36% of benzylfructoside and the increase in the copper reductions was expressed as a percentage of the maximum hydrolysis *caused by the enzyme.* After 0.5, 1, 1.4, 1.75, 2.25, 3, 4, 5, 6, 8 and 10 minutes the hydrolysis was 29.6, 53.8, 68.9, 80.9, 88.7, 92.2, 95.5, 95.5, 96.7, 98.4 and 100%, respectively (Fig. 2, Curve C). The corresponding velocity coefficients, calculated for a unimolecular reaction, increased from $10^4K = 50.8$ (0.5 min.) to $10^4K = 70.1$ (2.25 min.) and subsequently diminished.[13]

TABLE IV

PARTIAL ENZYMOTIC HYDROLYSIS OF A GAMMA-BENZYL FRUCTOSIDE MIXTURE. OPTICAL ROTATIONS AT 23°[a]

Min.	V.°, obsd.	$[\alpha]^{23}_D$	Min.	V.°, obsd.	$[\alpha]^{23}_D$
0	+1.98[b]	+7.3	8.2	0.36	1.3
1	2.71	9.9	10	+ .06	+0.2
1.7	2.76	10.1	14	− .43	−1.6
2.2	2.76	10.1	15	− .50	−1.9
2.7	2.58	9.5	19	− .69	−2.5
3.3	2.26	8.3	22	− .86	−3.1
4	1.96	6.9	25	− .79	−2.9
4.4	1.68	6.1	26.3	− .84	−3.1
5	1.48	5.4	27	− .84	−3.1
5.7	1.16	4.3	35	− .89	−3.3
7	0.73	2.7	1200[c]	− .87	−3.2

[a] See Fig. 2, Curve B. [b] Observed separately in absence of enzyme. [c] The solution had an acidity of *p*H 4.4 and the enzyme still actively hydrolyzed added sucrose.

Specific Rotations of the Benzyl Derivatives Hydrolyzed and Unhydrolyzed by Invertase.—The initial solution after dilution with an equal volume of enzyme had a dextrorotation of +1.98° in a 4-dm. tube and a reduction of 0.195% as fructose. At the end of the enzymotic hydrolysis the levorotation was −0.87°, observed in a 4-dm. tube, and the corresponding reduction was 0.705%. Further hydrolysis with 0.33 *N* hydrochloric acid at 23° reduced the rotation to −16.49° (L = 4) and increased the reduction to 1.575%, corresponding to a correct specific rotation of −90.6° for the fructose produced. These data, in conjunction with the fact that a 1% solution of the ketose in water at 23° had a levorotation of −10.40° (L = 4), made it possible to calculate[2a] that the specific rotation of the benzyl derivative hydrolyzed by invertase was −27.7° in water while a rotation of +41.0° could be assigned to the non-reducing benzylfructofuranosides stable to the enzyme. These specific rotations were found to be −27.4° and +40.0°, respectively, in an independent experiment carried out at 20°.

The molar composition of the gamma-benzyl fructoside mixture isolated from the acid benzyl alcohol near point A (Fig. 2, Curve A) was also calculated to be approximately: fructose in a reducing condition, 12.4%; non-reducing derivative hydrolyzed by invertase, 32.4% and non-reducing derivatives stable to invertase, 55.2%. The derivative hydrolyzed by invertase was 0.0283 molar in the solution examined.

Comparative Enzymotic Hydrolysis of Sucrose.—The same invertase solution as used above was mixed at 23°

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(13) See preparation of tetraacetyl α-benzyl- from α-methylfructofuranoside.

with an equal volume of an aqueous 1.938% sucrose solution carefully buffered to *p*H 4.4. The copper reduction of the resulting 0.0283 *M* mixture was plotted against time and the unimolecular velocity constants were calculated for 30, 40, 50, 60, 70, 80, and 90% inversion. These constants were, respectively, 5.31, 5.50, 5.31, 4.89, 4.74, 4.72, and 5.39 times greater than those determined at similar stages in the enzymotic hydrolysis of the gamma benzylfructoside mixture. Invertase therefore hydrolyzed a constituent in the latter approximately 5.1 times more slowly than sucrose.

One of the authors (C. B. P.) desires to thank the Chemical Foundation of New York for a Research Associateship.

Summary

1. Crystalline α-methylfructofuranoside, m. p. 80.5–81° and $[\alpha]^{20}\text{D}$ +93.0° in water, gave a new crystalline tetraacetate, m. p. 48–48.5° and $[\alpha]^{20}\text{D}$ +88.1° in chloroform, which was also prepared directly from sucrose.

2. An unstable, amorphous α-methyl glycoside–hydrogen chloride addition compound was precipitated when the constituents were mixed in anhydrous dioxane. The course of the subsequent decomposition was followed in more dilute solution both polarimetrically and by means of the copper reducing power. The behavior of gamma-fructosides dissolved in acid alcohols was in consequence assumed to depend on the formation of reducing, chlorine-containing substances which underwent change prior to their re-condensation with the solvent.

3. α-Methylfructofuranoside, when dissolved in benzyl alcoholic hydrogen chloride, was replaced very rapidly by a mixture of benzyl gammafructosides. Pure α-benzylfructofuranoside, m. p. 89°, $[\alpha]^{20}\text{D}$ +45.7° in water, was isolated from this mixture in the form of its crystalline tetraacetate, m. p. 84.5–85°, $[\alpha]^{20}\text{D}$ +64.7° in chloroform. Aqueous acid hydrolyzed the unsubstituted α-benzyl glycoside 16.5 times more rapidly than sucrose but it was unaffected by invertase.

4. Benzyl alcoholic hydrogen chloride partially converted α-benzylfructofuranoside into another non-reducing benzyl derivative of gammafructose which was not isolated. This benzyl derivative was hydrolyzed by invertase 5.1 times more slowly than sucrose. It had a specific levorotation of $[\alpha]^{20}\text{D}$ $-27 \pm 2°$ in water, calculated on the assumption that it possessed the molecular weight of a true benzylfructoside.

5. The constitutions of the crystalline α-methyl- and α-benzylglycosides described above were established by the methylation method. Tetramethyl α-benzyl- and α-methylfructofuranosides were liquids with refractive indices of $n^{19}\text{D}$ 1.4900 and $n^{20}\text{D}$ 1.4417, respectively, and with specific dextrorotations in chloroform of $[\alpha]^{19}\text{D}$ +83.3° and $[\alpha]^{20}\text{D}$ +115.9°, respectively. Both gave tetramethyl fructofuranose when hydrolyzed with aqueous acid.

6. Fear and Menzies' method of methylation with thallous ethylate and methyl iodide gave satisfactory results in the preparations described in (5).

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

The Cleavage of Side Chains in Aromatic Hydrocarbons in the Form of Paraffins by Means of Aluminum Chloride[1]

BY V. N. IPATIEFF AND HERMAN PINES

In the course of the study of polymerization of olefins,[2] alkylation[3] and depolyalkylation[4] of aromatic hydrocarbons, one of the chief difficulties in the identification of the reaction products was the lack of an adequate method for determining the structure of the alkyl group attached to the aromatic ring. It was tried[5] by a destructive hydrogenation method to convert the alkyl group to the corresponding paraffinic hydrocarbon. It was possible by this method to obtain methane and benzene from toluene; ethane and benzene from mono- and polyethylbenzene. However, in the case of propyl and butylbenzenes, the alkyl group was decomposed yielding methane, ethane and some propane. The

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at Pittsburgh, September 7–11, 1936.

[2] Ipatieff and Pines, *J. Ind. Eng. Chem.*, **27**, 1364 (1935); **28**, 684 (1936).

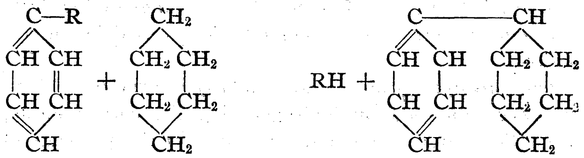
[3] (a) Ipatieff, Pines and Komarewsky, *ibid.*, **28**, 222 (1936); (b) Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936); (c) Ipatieff, Komarewsky and Pines, *ibid.*, **58**, 918 (1936).

[4] Ipatieff and Pines, *ibid.*, **58**, 1056 (1936).

[5] Ipatieff and Pines, in publication.

destructive hydrogenation method, therefore, could not be used for the identification of alkylated aromatic hydrocarbons.

During the study of the behavior of different hydrocarbons in the presence of aluminum chloride, it was decided to investigate whether an alkyl group in an alkylated benzene could migrate and attach itself to cyclohexane to give alkylcyclohexane. The migration of alkyl groups from aromatics to naphthenes was not observed to take place. An interesting fact, however, was noticed, namely, when an alkylbenzene is heated with cyclohexane, the alkyl group is split off to yield the corresponding paraffin. Propyl-, *s*-butyl-, *t*-butyl- and *t*-amylbenzene when heated with cyclohexane in the presence of aluminum chloride yield, respectively, propane, butane, isobutane and isopentane. The hydrogen necessary to hydrogenate the alkyl group to the corresponding paraffin comes from the interaction of the two cyclic compounds: aromatic and naphthenic. This could be written schematically as follows



Isopropylbenzene alone does not yield propane under similar conditions; tertiary butylbenzene, however, yields isobutane and high boiling products.

The reaction written above is not the only one which occurs. In the case of isopropylbenzene and cyclohexane, besides propane and phenylcyclohexane, the following products were identified: methylcyclopentane, benzene, *p*-diisopropylbenzene and a product corresponding to cyclohexylisopropylbenzene or methylcyclopentylisopropylbenzene.

The yield of paraffin gases formed from the cleavage of aromatic side chains depends on two factors: (1) the structure of the alkyl group, and (2) the ease with which the cycloparaffin gives off hydrogen.

It was found that the alkyl group of isopropylbenzene splits off with more difficulty in the presence of monosubstituted cyclohexane than in the presence of cyclohexane; disubstituted cyclohexanes such as *p*-methylisopropylcyclohexane do not cause the cleavage of the alkyl groups in isopropylbenzene. Semi-quantitative determinations have shown that the ease of cleaving the isopropyl group from isopropylbenzene decreases with the substitution in the cyclohexane ring.

It was found that decahydronaphthalene facilitates the cleavage of the alkyl group in alkylated benzene. The product obtained from this reaction contains among others a compound corresponding to decahydronaphthylbenzene, which shows the origin of the hydrogen necessary to reduce the alkyl groups to paraffin.

The following tabulation gives the approximate yield of paraffin formed from the reaction between alkylated aromatics with cyclohexane and decahydronaphthalene.

		Naphthene hydrocarbon used	
		Cyclohexane	Decahydronaphthalene
	Paraffin formed		
Aromatic hydrocarbon used	Kind	Yield, %	Yield, %
Toluene	None	0	0
Ethylbenzene	None	0	0
Isopropylbenzene	Propane	33	53
s-Butylbenzene	Butane	35	71
t-Butylbenzene	Isobutene	61	94
s-Amylbenzene	Isopentane	60	..

The above tabulation shows that a tertiary butyl group splits off more easily than a secondary butyl group and that the latter splits off still more easily than an isopropyl group. Ethyl and methyl groups do not split off under the same conditions. The relative instability of the alkyl groups attached to the benzene ring is the same as that which we would predict from Kharasch's table of the relative electro-negativity of organic radicals.[6]

The method of cleaving alkyl groups from aromatic hydrocarbons could serve as a means for a direct measurement of the relative stability of the bond between the alkyl and phenyl radicals in alkylated aromatic hydrocarbons; it would also be possible to determine by this method the effect of different substituents on the relative stability of this bond. This method could also be used for direct measurement of the relative stability of the carbon–hydrogen bond in cyclic compounds like cyclohexane, decahydronaphthalene and possibly in some paraffinic hydrocarbons. By this method it was found that substitution increases the stability of the carbon–hydrogen bond in the cyclohexyl ring. The tabulation given above has also demonstrated that the carbon–hydrogen bond in decahydronaphthalene is less stable than in cyclohexane.

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(6) (a) Kharasch and Grafflin, THIS JOURNAL, **47**, 1948 (1925); (b) Kharasch and Marker, *ibid.*, **48**, 3130 (1926); (c) Kharasch and Flenner, *ibid.*, **54**, 674 (1932).

An important application of the above mentioned reaction is its use in determining the structure of alkyl groups attached to an aromatic nucleus. It is important to keep the temperature of the reaction below 80°, since at higher temperatures partial decomposition of the hexamethylene ring to isobutane takes place.

It is worth while to mention here that alkylated cyclohexane when treated under similar conditions with cyclohexane or benzene does not yield paraffinic hydrocarbons. It seems that alkyl groups are much more strongly attached to a hexamethylene ring than to a phenyl ring.

In order to split the side chains from alkylnaphthenes, it is necessary to raise the temperature to 90° or higher; under these conditions, however, the hexamethylene ring decomposes, yielding isobutane.

The same type of reaction as mentioned above takes place when olefins are treated with benzene in the presence of cyclohexane or decahydronaphthalene and aluminum chloride. It seems that alkylation of aromatic hydrocarbons takes place first, which in the presence of cyclohexane dealkylate to give paraffins. *n*-Butene under these conditions yielded *n*-butane, while diisobutene or di-*n*-butene yielded isobutane. The last two experiments show that under these conditions depolyalkylation has taken place. In the case of di-*n*-butene, the depolyalkylation was accompanied by isomerization. The detailed results obtained from the action of olefins on cyclic hydrocarbons will be reported in another paper.

The reactions described in this paper are intended to be studied with other alkylating and polymerizing catalysts.

Apparatus and Procedure.—The apparatus consisted of a 250-cc. flask provided with a dropping funnel, mercury sealed stirrer, reflux condenser and an inlet tube for the hydrogen chloride. Ground glass joints were used throughout. The gases formed were collected in a calibrated trap (100-cc. capacity) cooled to −78° by means of a mixture of carbon dioxide and acetone. The non-condensable gases, if any, were collected in a gas bottle over salt water.

Aluminum chloride and the naphthene or decahydronaphthalene were placed in the flask, and a stream of nitrogen was passed to sweep out the air; a slow stream of hydrogen chloride was passed in and the flask was heated to the desired temperature by means of a water-bath. The aromatic hydrocarbons were then introduced. The gases evolved were submitted to a fractional distillation in a low temperature Podbielniak apparatus. The contents of the flask after the reaction consisted, in most cases, of two layers; the upper hydrocarbon layer was washed with 10% solution of sodium hydroxide followed by water, dried over calcium chloride and distilled. The lower aluminum chloride layer was decomposed with ice, neutralized with sodium hydroxide solution, dried and distilled.

Materials.—Toluene, xylenes, ethylbenzene and cyclohexane were obtained from the Eastman Kodak Company.

Isopropylbenzene, *s*-butylbenzene, *t*-butylbenzene and *s*-amylbenzene were obtained by treating propene, *n*-butene, isobutene and isopropylethylene, respectively, with benzene using 96% sulfuric acid as the catalyst.[7] In the case of alkylation of benzene with the last two olefins, the chief product formed was the dialkylbenzene which was dealkylated to the mono-substituted benzene by treating it with benzene in the presence of ferric chloride.[8] The aromatic hydrocarbons used had the following boiling ranges and indices of refraction:

Hydrocarbon	B. p., °C.	n^{20}D
Isopropylbenzene	151–152	1.4922
s-Butylbenzene	170–171	1.4901
t-Butylbenzene	168–169	1.4912
s-Amylbenzene	188–190	1.4932

Decahydronaphthalene was obtained from the Eastman Kodak Co. This product was stable toward a nitrating mixture, indicating the absence of naphthalene or tetrahydronaphthalene. The product was redistilled several times and the fraction having a boiling range of 187–189° and index of refraction n^{20}D of 1.4745 was used for the reaction.

Isopropylcyclohexane and *p*-methylisopropylcyclohexane were obtained by hydrogenating the corresponding aromatic hydrocarbons under pressure in the presence of nickel.

Experimental Data.—The conditions under which the experiments were carried out and the results obtained are given in Table I.

As an example of the type of products which are obtained, two experiments will be discussed in detail.

Experiment No. 4. Isopropylbenzene-Cyclohexane-Aluminum Chloride-Hydrogen Chloride. Hydrocarbon Layer.—The boiling range of the hydrocarbon layer was as follows:

B. p., °C.	% by weight
76–80	54
150–200	14
200–250	20
250–285	8
Above 285	3

The different products were redistilled and the following fractions isolated.

Fraction 76–80° contains 13.5% of benzene. This was determined by treating the fraction with fuming sulfuric acid (15% SO_3). The remaining compounds consisted of cyclohexane with pure methyl cyclopentane.

Fraction 140–166°, n^{20}D 1.4909, was completely soluble in 15% fuming sulfuric acid. This indicates the absence of alkyl cyclohexane.

Fraction 202–204°, n^{20}D 1.4907, corresponds to *p*-diisopropylbenzene. Calcd. for $C_{12}H_{18}$: C, 88.89; H, 11.11; mol. wt., 161. Found: C, 88.77; H, 11.18; mol. wt., 162.

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[7] Ipatieff, Corson and Pines, This Journal, **58**, 919 (1936).

[8] Ipatieff and Corson, unpublished results.

TABLE I

Expt. no.	Aromatic hydrocarbons used	Am., g.	Cyclohexane, g.	$AlCl_3$	Conditions of reactions		Results				
							Gas found			Hydroc. layer	$AlCl_3$ layer
					Temp., °C.	Time, hrs.	cc.	Kind	%		
1	Toluene	55	75	25	67–82	4:15	[a]			51.8	102
2	Xylene	48.5	57.5	25	67–80	3:15	[a]			84.6	96.7
3	Ethylbenzene	48	57	23	70–80	3:25	[a]			75.7	97.8
4	Isopropylbenzene	36	37.8	10	80	3:00	2400	Propane	96	51.5	27.5
5	*p*-Diisopropylbenzene	48.6	54.3	15	80	3:15	2600	Propane	96	79.1	31.2
6	*s*-Butylbenzene	40	38	10	80	3:00	2300	*n*-Butane	100	51.8	25.7
7	*t*-Butylbenzene	40	38	10	70	1:00	4000	*i*-Butane	100	..	..
8	*s*-Amylbenzene	44	38	15	65–82	2:00	Liq. 17 cc.	*i*-Pentane	100	40.9	40.4
			Decahydronaphthalene								
9	Isopropylbenzene	36	62	15	80	3:00	3610	Propane	98	69.7	37.0
10	*s*-Butylbenzene	40	62	15	80	3:00	4790	*n*-Butane	98	69.4	38.6
11	*i*-Butylbenzene	40	62	15	60–78	1:15	6450	*i*-Butane	98	57.9	46.4

[a] Negligible amount of methane and ethane was formed.

The oxidation of the fraction by means of dilute nitric acid (1:2.5) yielded terephthalic acid, which when converted to dimethyl terephthalate yielded a crystalline product with a melting point of 138°.

Fraction 239–245°, $n^{20}D$ 1.5191, probably contains a mixture consisting of triisopropylbenzene and phenylcyclohexane or phenylmethylcyclopentane. Calcd. for C_6H_5-C_6H_{11}: C, 90.0; H, 10.0; mol. wt., 184; $n^{20}D$, 1.5275. Calcd. for $C_6H_3(C_3H_7)_3$: C, 87.9; H, 12.1; mol. wt., 204; $n^{20}D$, 1.4929. Found: C, 89.3; H, 10.42; mol. wt., 174. On the basis of organic analysis and molecular weight determinations and index of refraction, it seems that the product consists of a mixture composed of 30% triisopropylbenzene and 70% of phenylcyclohexane.

Use of the dehydrogenation method, conversion of phenylcyclohexane to diphenyl is contemplated for proving the presence of the latter.

Fraction 275–280°, $n^{20}D$ 1.5170, corresponds to isopropylcyclohexylbenzene. Calcd. for $C_3H_7C_6H_4C_6H_{11}$: C, 89.11; H, 10.89; mol. wt., 202. Found: C, 89.19; H, 10.92; mol. wt., 207.

Catalyst Layer.—The aluminum chloride layer after being decomposed, washed and dried, weighed 11 g. It was submitted to a fractional distillation.

B. p., °C.	% by weight
75–78	27
78–148	6
148–250	19
250–315	21
315–360	10
Above 360	12

The index of refraction of the different fractions corresponded very closely to the index of refraction of the hydrocarbon layer.

Fraction 275–285°, $n^{20}D$ 1.5232, corresponds to isopropylcyclohexylbenzene. Calcd. for $C_3H_7C_6H_4C_6H_{11}$: C, 89.11; H, 10.89; mol. wt., 202. Found: C, 89.50; H, 10.42; mol. wt., 206.

Experiment 11. *t*-Butylbenzene-Decahydronaphthalene-Aluminum Chloride-Hydrogen Chloride. Hydrocarbon Layer.—After washing and drying it weighed 51.05 g. The following is the distillation range of the product.

B. p., °C.	% by weight
82–94	9.6
94–160	1.5
160–200	54.5
200–250	6.0
250–320	20.0
Bottoms	8.4

On redistillation the several fractions were separated.

Fraction 82–94° consisted of benzene.

Fraction 185–190°, $n^{20}D$ 1.4697, stable toward a nitrating mixture; organic analysis shows that it corresponds to decahydronaphthalene. Calcd. for $C_{10}H_{18}$: C, 86.97; H, 13.04; mol. wt., 138. Found: C, 87.14; H, 13.14; mol. wt., 136.

The index of refraction of this fraction was lower than that of the original product. This indicates that isomerization has taken place. Whether this is the case of *cis-trans* isomerization or whether the six-membered rings isomerize into five-membered rings as in the case of cyclohexane, is being investigated.

Fraction 300–310°, $n^{20}D$ 1.5330. This product corresponds to decahydronaphthylbenzene. Calcd. for $C_{10}H_{17}$-C_6H_5: C, 89.72; H, 10.28; mol. wt., 214. Found: C, 89.38; H, 10.62; mol. wt., 205; d^{20}_4, 0.9696.

Aluminum Chloride Layer.—The catalyst layer was decomposed, washed, dried and distilled.

B. p., °C.	% by weight
80–90	10.5
90–180	5.0
180–230	15.5
230–330	7.4
Bottoms	62.1

The product was redistilled and the index of refraction of the different fractions is the same as for the corresponding ones of the upper layer.

Acknowledgment.—The authors thank Mr. Bruno Kvetinskas for assistance in the experimental work.

Summary

When alkylbenzenes are heated with cyclohex-

ane or decahydronaphthalene in the presence of aluminum chloride catalyst, the alkyl groups are split off to yield the corresponding paraffins.

The relative stability of different alkylbenzenes is reported.

Various applications of this reaction are proposed.

RIVERSIDE, ILL. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Thermal Decomposition of Gaseous Silicon Tetramethyl

BY DAVID F. HELM AND EDWARD MACK, JR.

In a previous paper[1] a study was made of the thermal decomposition of gaseous germanium tetraethyl. In the present paper the same type of study has been made of silicon tetramethyl. We have found that silicon tetramethyl gives a homogeneous decomposition which is unimolecular down to pressures of about 10 cm. In the case of germanium tetraethyl, over the temperature range employed, 420–450°, the products of the decomposition were a bright mirror-like deposit of germanium on the walls of the reaction vessel and a gas phase of essentially the same composition as the products obtained from the pyrolysis of *butane* at these temperatures. Whereas in the case of the more stable silicon tetramethyl it was necessary, to obtain a conveniently measurable rate of decomposition, to work at a much higher temperature, 660–720°, a sooty deposit was formed, consisting of silicon *and carbon*, and the gaseous products resembled closely those obtained from the pyrolysis of *ethane* at these temperatures.

Experimental

Silicon tetramethyl was prepared with the Grignard reaction by a method analogous to that employed[2] by Dennis and Hance for making germanium tetramethyl. The fraction of the purified product saved for use had a boiling point of 26.30 ± 0.05°.

The course of the decomposition was followed by three different manometer techniques, all of which gave substantially the same results. These included (1) a direct manometric method which was later abandoned in favor of (2) pointer membrane manometers and (3) clicker type null pressure gages. The pointer manometers were used in the same way as those described by Geddes[1] and Mack. Clicker gages were mounted outside the furnace and connected to the reaction vessel and the manometer line in the usual manner.

In the fairly high temperature range, 660–720°, it was necessary that fuzed quartz reaction chambers be used rather than Pyrex. Constant temperature inside a heavily lagged electric furnace was maintained within 0.3° with a platinum resistance thermometer wound near the heating coils and with an automatic controlling mechanism similar to that described by Scott and Brickwedde.[3]

Treatment of Data

The data for a typical run (No. 33) are given in Table I. This decomposition was carried

TABLE I

DATA FOR VELOCITY CONSTANT AT 678.7°

Time, min.	Pressure (P), cm.	$P_\infty - P$	k, sec.$^{-1}$	
Before	10.35			
0	33.00 = P_0			
3.62	38.35	58.45		
4.55	42.30	54.50	0.00126	
5.28	45.70	51.10	.00147	
6.00	48.64	48.16	.00137	
7.03	52.60	44.20	.00139	
7.92	55.70	41.10	.00137	
9.07	59.35	37.45	.00135	Av. 0.00133 0.4 to 0.8 completed
10.02	62.13	34.67	.00135	
11.25	65.45	31.35	.00136	
12.48	68.37	28.43	.00132	
13.75	71.10	25.70	.00133	
14.92	73.35	23.45	.00131	
16.07	75.45	21.35	.00136	
17.50	77.73	19.07	.00131	
19.35	80.32	16.48	.00132	
20.65	81.91	14.89	.00130	
22.08	83.50	13.30	.00132	
23.55	84.95	11.85	.00131	
25.17	86.40	10.40	.00134	
27.20	87.90	8.90	.00128	
28.62	88.85	7.95	.00132	
31.05	90.22	6.58	.00130	
33.12	91.20	5.60	.00129	
37.08	92.66	4.14	.00127	
42.06	94.05	2.75		
92.00	96.80 = P_∞			
After run	31.15	$P_\infty / P_0 = 2.95$		

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(1) Geddes and Mack, THIS JOURNAL, **52**, 4372 (1930).

(2) Dennis and Hance, *J. Phys. Chem.*, **30**, 1055 (1926).

(3) Scott and Brickwedde, *Bur. Standards J. Research*, **6**, 407 (1931).

through at 678.7° with a membrane manometer. Inspection of the velocity constants computed from the time intervals shows that, after temperature equilibrium had been established, deviations are reasonably small. There is a small but definite drift downward in the value of the velocity constant toward the end, as is usually observed in such reactions. It is probably to be ascribed, at least in part, to the effect of the relatively large proportion of products on the small fraction of remaining silicon tetramethyl.

It was our uniform practice to compute the velocity constant for the interval from 0.4 to 0.8 completed and to consider this the constant for the run. The velocity constant for run No. 33 in Table I consequently is taken as 0.00133 sec.$^{-1}$. The ratio of the pressures (room temperature) before and after the decomposition was found to be 3.01; its close equivalent, P_∞/P_0, was 2.95.

Table II gives data for decompositions, at various pressures, all carried out at 689°. The method employed is given as (P) for pointer membrane and (C) for clicker system.

TABLE II

DATA FOR DECOMPOSITIONS AT 689°

Run	Method	P_0, cm.	P_∞/P_0	k, sec.$^{-1}$	
2	P	43.8	2.98	0.00188	Av. 0.00198
4	P	27.0	2.61	.00203	
8	P	25.1	3.00	.00210	
9	P	36.8	2.87	.00180	
10	P	32.5	2.92	.00193	
11	P	34.6	2.87	.00193	
16	P	23.1	3.03	.00202	
52	P	35.5	2.90	.00188	
51	P	15.3	3.20	.00212	
47	P	13.5	2.98	.00220	
75	C	12.6	..	.00182	
46	P	7.8	3.45	.00215	
76	C	7.7	..	.00188	
77	C	7.5	..	.00193	
45	P	7.4	3.25	.00222	
78	C	6.9	..	.00205	
50	P	5.8	2.79	.00217	
44	P	4.0	3.89	.00232	
79	C	3.68	..	.00200	
42	P	3.58	3.95	.00245	
80	C	3.3	..	.00198	
43	P	3.12	3.39	.00233	
81	C	1.48	..	.00210	
82	C	1.22	..	.00215	
49	P	0.85	..	.00225	
83	C	.44	..	.00207	
13	P	27.3	2.93	.00195	Av. 0.00204 (Surface increased 40–50 times)
14	P	25.7	3.46	.00212	
15	P	33.8	3.42	.00205	

The separate velocity constants calculated over short time intervals during any one decomposition are in fairly good agreement if the initial pressure, P_0, is high, and show a falling off only in the last quarter of the run. When the initial pressure is low the constants show a rapid falling off during the run, indicating that a unimolecular reaction is not being followed strictly. This second type of behavior begins to be apparent in the vicinity of 10 cm. initial pressure. A final average for the unimolecular constant is taken for P greater than 13 cm. (Below 10 cm. initial pressure the average k for a run was close to that for higher pressures but it was the mean of a rapidly descending series of values.) No critical pressure could be found below which the specific reaction rate was even reasonably constant throughout the run and lower than that secured at high pressures. The break predicted by the Lindemann theory seems lost as the unimolecular rate fades gradually into a higher order reaction with decreasing pressure.

At the bottom of Table II, the complete homogeneity of the reaction is shown by the results of Runs 13, 14, 15, in which the exposed surface area in the reaction vessel was increased 40–50 times by addition of quartz fibers, without a significant change in the velocity constant. A wall reaction may well play a significant role at low pressures, however.

The data for a typical low pressure run are

TABLE III

TYPICAL DECOMPOSITION AT LOW PRESSURE (689°)

Time, min.	Pressure, P	$P_\infty - P$	k, sec.$^{-1}$ Unimolecular	k', sec.$^{-1}$ Bimolecular
0	14.9 = P_0			
3.25	26.60	18.00		
4.12	29.05	15.55	0.0028	0.00017
5.33	31.70	12.90	.0026	.00018
6.35	33.45	11.15	.0024	.00019
7.60	35.30	9.30	.0024	.00023
8.78	36.50	8.10	.0020	.00027
10.27	37.80	6.80	.0020	.00026
11.78	38.75	5.85	.0017	.00026
14.33	40.05	4.55	.0015	.00032
16.78	40.83	3.77	.0013	.00031
19.08	41.45	3.15	.0013	.00038
22.43	41.98	2.62	.0009	
26.42	42.58	2.02	.0011	
31.10	42.87	1.73	.0006	
39.30	43.45	1.15		
43.50	43.60			
54.00	43.97			
74.42	44.35			
97.0	44.60 = P_∞			

given in Table III. The data were secured with a clicker system and a heavy walled quartz reaction vessel to avoid appreciable loss of hydrogen by diffusion. Pressures were measured in cm. of ethyl phthalate and the initial pressure (P_0) is taken as $^1/_3\ P_\infty$ or 14.9 cm. ethyl phthalate or 1.22 cm. of mercury.

Velocity constants when computed on both a uni- and a bimolecular basis are about equally unsatisfactory, and indicate an order of reaction between the two.

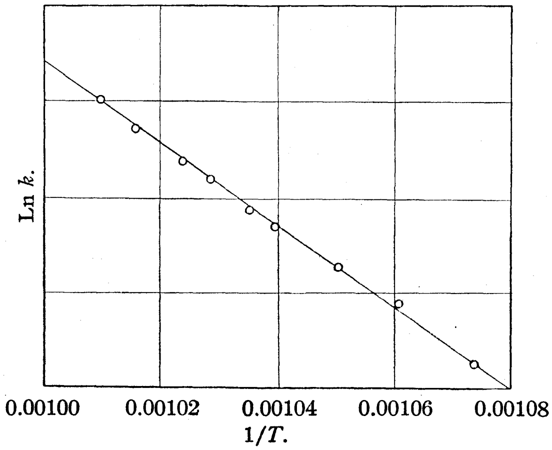

Fig. 1.

The variation of the velocity constant with temperature is shown in Table IV, and the plot of ln k against $1/T$ is given in Fig. 1.

Table IV

Temperature Coefficient Data

No. of runs	Temp., °C.	Av. k, sec.$^{-1}$
3	717	0.00672
3	711	.00520
3	704.6	.00380
10	700	.00320
13	693	.00233
10	689	.00198
6	679	.00134
5	669.2	.000847
3	659	.000527

The velocity constant as a function of temperature is given by the equation

$$\ln k = 35.03 - 78{,}800/RT$$

The energy of activation for the reaction is hence 79,000 cal. with a possible error of several thousand calories.

Analysis of Gaseous Products

In three cases after decomposition had been completed the vapor phase was pumped off and analyzed in a modified Bone–Wheeler apparatus. The results are given in Table V.

Table V

Analysis of Products

Compound	Temp., of decp., °C.	Acetylenes	Olefins	Hydrogen	Methane	Ethane	Time, min.
Si(Me)$_4$	659	0.75	1.5	39.2	58.4	0.0	180
Si(Me)$_4$	689	.13	1.0	40.0	58.8	.0	70
Si(Me)$_4$	689	.52	0.0	39.1	60.4	.0	70
Ethane	675	1.9	.7	40.9	54.5	2.0	360
Ethane	810	0.5	.75	34.10	65.65	0.0	15

For comparison the table includes the analyses of Bone and Coward[4] on the products resulting from the pyrolysis of ethane. If Si(Me)$_4$ decomposes through the agency of free methyl radicals, these short-lived molecules would come out of the reaction energy-loaded and in a highly reactive condition. It appears plausible that they might unite to form ethane but only momentarily, for ethane is known to decompose rapidly at these temperatures. The similarity of the products from ethane and Si(Me)$_4$ suggests that such a mechanism may be possible.

Summary

The thermal decomposition of silicon tetramethyl has been studied in the temperature range 659–717° and found to be homogeneous and unimolecular at pressures above 10 cm., and to fade into a higher order reaction at lower pressures.

The energy of activation is about 79,000 cal. and the velocity constant is given by the equation

$$\ln k = 35.03 - 78{,}800/RT$$

(In the case of germanium tetraethyl, the equation is $\ln k = 28.79 - 51{,}000/RT$, when k is expressed in reciprocal seconds.)

The decomposition produces a deposit of carbon and silicon and a gas phase essentially that secured upon pyrolysis of ethane.

No Lindemann critical pressure between uni- and bi-molecular rates could be located.

Chapel Hill, N. C. Received November 2, 1936

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[4] Bone and Coward, *J. Chem. Soc.*, **93**, 1206 (1908).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Rate of Dissolution of Magnesium in Acids

BY CECIL V. KING AND WILLIAM H. CATHCART

As the result of previous studies in this Laboratory, the conclusion was reached that the rate of dissolution of magnesium in acids which are neither extremely weak nor form slightly soluble magnesium salts, is controlled by the rate of convection (stirring) and by the rate of diffusion of the acid.[1-3] It has been pointed out that the theory of Nernst[4] must be modified, in that the "diffusion layer" cannot be a stagnant layer (or even a layer in which flow is laminar only), and that the thickness of this layer must vary with the diffusion coefficient of the reagent, increasing as the latter increases. Investigators in related fields have concluded that in such processes the concentration gradient near the surface is not even linear, and that there may be a wide zone in which both diffusion and convection aid in the transport of material to and from the surface.

An entirely different picture of the dissolution process has been proposed by Kilpatrick and Rushton.[5] These authors have tried to show that the rates are dependent on the acid strength, in the same manner as in homogeneous acid–base catalysis; *i. e.*, that

$$k_{\mathrm{A}} = GK_{\mathrm{A}}^{x}$$

where k_{A} is the dissolution rate constant, K_{A} the acid dissociation constant, G and x are numerical constants, the latter a proper fraction. This assumes that the rate is controlled by the chemical reaction velocity and is entirely independent of diffusion rates.

This viewpoint has been criticized before,[1-3] but it is true, as Kilpatrick and Rushton pointed out, that it has been impossible to make a satisfactory comparison of the dissolution rate constants and the meager list of diffusion coefficients to be found in the literature. For this reason it was decided to determine the diffusion coefficients of a number of weak and strong acids, in the presence of their magnesium salts (when possible), and make the comparison with dissolution rate constants determined, so far as practical, under the same conditions of reagent and salt concentration.

It was found impossible to use the dissolution rate data of Kilpatrick and Rushton in this comparison, for several reasons. First, the great variation in diffusion coefficient with salt concentration in the case of strong acids makes it necessary to know the coefficient and rate constant in the presence of sufficient salt so that the salt formed in the reaction has little or no further effect. Second, Kilpatrick and Rushton do not report the actual rate constants obtained with certain acids (tartaric, citric, bisulfate, sulfuric) but hypothetical constants calculated for the undissociated acids in these solutions. Third, consistently lower dissolution rates were found in all acids than by these authors, although every effort was made to use comparable conditions.

Consequently, dissolution rate measurements were made in the same acids whose diffusion coefficients were measured, in the presence of the same salts. With the exception of benzoic, all the acids were ones used by Kilpatrick and Rushton.

Experimental

Diffusion Rates.—Measurements were made in porous glass disk cells of the type described by McBain and Dawson;[6] in a few cases the rotating cells described by Mouquin and Cathcart[7] were used. In general, the stationary and rotating cells gave nearly the same values in the critical concentration range. Diffusion coefficients (D) were calculated as described in another paper.[8] All measurements were made at 25 ± 0.02°. Most of the measurements have an estimated accuracy of about ±1%.

In all experiments the acid concentration was near 0.05 N initially except in the case of benzoic acid. The exact concentration before and after a twenty-four- to sixty-hour run was determined in terms of a standard alkali solution, and sometimes the acid diffusing through the cell disk was determined as well. The added salt had the same concentration on both sides of the disk initially; no attempt was made to follow its movement. Conditions within the "diffusion layer" of the dissolution rate experiments can only be approximated within the cell disk at best; but, as will be seen below, certain salt concentrations allow the best comparison available.

The results of the diffusion rate measurements are summarized in Table I and shown graphically in Fig. 1. The values of D are given in cm.^{2}/min. since the dissolution rate constants were calculated in cm./min. The effect of

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(1) King and Braverman, THIS JOURNAL, **54**, 1744 (1932).

(2) King, *ibid.*, **57**, 828 (1935).

(3) King and Schack, *ibid.*, **57**, 1212 (1935).

(4) Nernst, *Z. physik. Chem.*, **47**, 52 (1904).

(5) Kilpatrick and Rushton, *J. Phys. Chem.*, **34**, 2180 (1930); **38**, 269 (1934); Kilpatrick, *J. Chem. Ed.*, **8**, 1567 (1931).

(6) McBain and Dawson, THIS JOURNAL, **56**, 52 (1934).

(7) Mouquin and Cathcart, *ibid.*, **57**, 1791 (1935).

(8) King and Cathcart, *ibid.*, **58**, 1639 (1936).

added salt is seen to divide the acids roughly into two groups: (a) the diffusion coefficients of strong acids are greatly increased by the magnesium salts and (b) the diffusion coefficients of weak to moderately strong acids are either little affected, slightly decreased or slightly increased by salt addition. Three points are worthy of note: magnesium chloride does not increase the diffusion coefficient of hydrochloric acid nearly as much as sodium chloride does;[8] sodium bisulfate and sulfuric acid have practically the same coefficients in the presence of magnesium sulfate; and some of the organic acids used have such slightly soluble (acid?) magnesium salts that sodium chloride was used as the added salt.

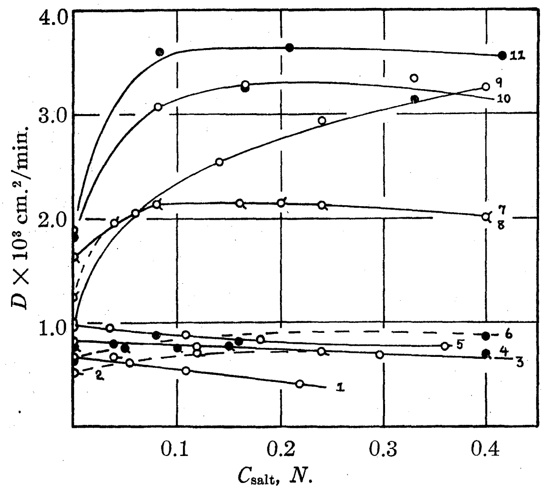

Fig. 1.—Diffusion coefficients *vs.* salt concentration. Acids: 1, benzoic; 2, citric (ɋ); 3, chloroacetic (○); 4, acetic (●); 5, formic; 6, tartaric; 7, bisulfate; 8, sulfuric; 9, benzene-sulfonic; 10, hydrochloric; 11, perchloric.

Dissolution Rates.—Magnesium cylinders approximately 2.6 cm. long and 1.8–2.0 cm. in diameter were rotated in 250 cc. of the acid solution contained in a 400-cc. beaker. The temperature of the solution was kept at 25 ± 0.5°, during the five- to fifteen-minute runs. The magnesium cylinders were carefully sanded to a smooth, clean surface before each series, and weighed before and after each run to the nearest 0.5 mg.

TABLE I

DIFFUSION COEFFICIENTS OF ACIDS WITH ADDED SALTS

25 ± 0.02°

Benzoic acid (0.01 *N*)
Sodium benzoate

C_{salt}, N	$D \times 10^3$ cm.²/min.	
0	0.665	0.665
	.679	
0.0438	.620	
.0548	.612	
.1097	.533	.541
.2190	.408	.418

Citric acid (0.05 *N*)
Sodium chloride

C_{salt}, N	$D \times 10^3$ cm.²/min.
0	0.513
0.04	.685
.12	.707
.24	.729
.40	.704
.60	.697

Monochloroacetic acid (0.05 *N*). Magnesium chloroacetate

0	0.838	0.829
0.119	.774	
.297	.695	
.593	.680	
1.188	.682	

Acetic acid (0.05 *N*)
Magnesium acetate

0	0.768	0.769
	.770	.783
0.050	.754	.782
.10	.762	
.15	.792	
.40	.710	
.10 NaCl	.826	.820
.20	.813	.826

Formic acid (0.05 *N*)
Magnesium formate

0	0.969	0.974
0.036	.962	
.108	.884	
.180	.845	
.360	.774	
.720	.677	

Tartaric acid (0.05 *N*)
Sodium chloride

0	0.657	0.648
0.04	.795	
.08	.870	
.16	.826	
.40	.872	

Sodium bisulfate (0.05 *N*)
(Normality = Molarity)
Magnesium sulfate

0	1.64
0.08	2.13
.16	2.14
.24	2.12
.40	2.02

Sulfuric acid (0.05 *N*)
Magnesium sulfate

0	1.24	1.26
0.04	1.95	
.08	2.11	
.20	2.14	
.40	2.02	

Benzenesulfonic acid (0.05 *N*)
Magnesium benzenesulfonate

0	0.986	1.07
0.06	2.06	
.14	2.54	
.24	2.94	
.40	3.26	
.80	3.31	

Hydrochloric acid (0.05 *N*)
Magnesium chloride

0	1.88	
0.082	3.07	
.165	3.28	
.330	3.35	
.659	2.27	2.22
.823	1.90	1.89
.165[a]	3.24	
.330[a]	3.15	
.823[a]	2.24	

Perchloric acid (0.05 *N*)
Magnesium perchlorate

0	1.82	1.84
0.083	3.59	
.208	3.64	
.416	3.56	
.832	2.93	

Pyridinium chloride (0.05 *N*)
0.05 *N* Pyridine both top and bottom of cell. Magnesium chloride

0	0.967	0.891[a]	0.915[a]
0.016	.815	.848[a]	
.08	.780	.767[a]	
.20	.698	.788[a]	
.40	.670	.762[a]	

[a] In rotating cell.

Velocity constants were calculated from the equation

$$k = \frac{2.3V}{At}\log\frac{a}{a - x}$$

where V = volume of solution in cc., A = area of surface in sq. cm., t = time of run in minutes, a = dissolving capacity of the solution in any units and x = amount dissolved in the same units as a. The values of k should thus be comparable with constants obtained by Kilpatrick and Rushton.

Since the latter authors either ran their experiments at, or calculated the constants to a surface (peripheral) speed of 2000 cm./min., all our experiments were run at this peripheral speed. For instance, a cylinder 2.54 cm. long, 1.99 cm. in diameter was rotated at 320 r. p. m. (=2000 cm./min.) for five minutes in 0.0516 *N* perchloric acid, and 24.0 mg. of magnesium was dissolved. The dissolving capacity of the solution was 157 mg. of magnesium. Then

$$k = \frac{2.3 \times 250}{15.8 \times 5} \log \frac{157}{157 - 24} = 0.524$$

As the cylinder diameter decreased, the rotational speed was increased to keep the peripheral speed at 2000 cm./min. A cylinder 2.64 cm. long and 1.86 cm. in diameter was rotated at 340 r. p. m. for five minutes in 0.0562 *N* sodium bisulfate and 22.5, 23.5 mg. of magnesium was dissolved. The dissolving capacity of the solution was 171 mg. of magnesium. Then as an average

$$k = \frac{2.3 \times 250}{15.4 \times 5} \log \frac{171}{171 - 23} = 0.468$$

No attempt was made to obtain greater accuracy than ±5%. The method of obtaining rates and calculating constants is given in detail because all our values of *k* are only one-third to one-half as large as those obtained by Kilpatrick and Rushton under presumably comparable conditions. We have found, as they also state, that *k* is independent of length or diameter of cylinder, volume of solution and concentration of acid. Hence we can only conclude that some "apparatus constant" was different in the two cases.

The results of the rate experiments are summarized in Table II and shown graphically in Fig. 2. Several points are worthy of note.

TABLE II

DISSOLUTION RATE CONSTANTS OF MAGNESIUM IN ACIDS WITH ADDED SALTS AT 25 ± 0.5°

Benzoic acid (0.02 *N*) Sodium benzoate

C_{salt}, *N*	$C_{\text{H}_2\text{O}_2}$, *M*	*k*	
0	0	0.200	0.195
0.20	0	0	
.40	0	0	
0	0.07	0.249	
.20	.07	.195	
.40	.07	.056	

Citric acid (0.055 *N*) Sodium chloride

C_{salt}, *N*	*k*
0	0.139
0.20	.146
.40	.146
.60	.154

Monochloroacetic acid (0.0518 *N*). Magnesium chloroacetate

C_{salt}, *N*	*k*	
0	0.273	0.250
0.121	.245	
.242	.223	
.362	.234	
.483	.213	
.604	.213	

Acetic acid (0.0597 *N*) Magnesium acetate

C_{salt}, *N*	*k*		
0	0.186	0.177	0.182
0.10	.177		
.20	.177		
.30	.182		
.40	.167		

Formic acid (0.0582 *N*) Magnesium formate

C_{salt}, *N*	*k*		
0	0.236	0.220	0.227
0.112	0.236		
.223	.225		
.335	.197		
.446	.197	0.173	

Tartaric acid (0.0621 *N*) Sodium chloride

C_{salt}, *N*	*k*		
0	0.172	0.172	0.177
0.20	.181		
.30	.172		
.40	.190		
.60	.181		

Sodium bisulfate (0.0562 *N*) (Normality = Molarity) Magnesium sulfate

C_{salt}, *N*	*k*	
0	0.457	0.480
0.20	.436	
.40	.414	

Sulfuric acid (0.0575 *N*) Magnesium sulfate

C_{salt}, *N*	*k*	
0	0.458	0.458
0.20	.447	
.40	.416	
.60	.396	

Benzenesulfonic acid (0.050 *N*) Magnesium benzenesulfonate

C_{salt}, *N*	*k*		
0	0.518	0.499	0.502
0.10	0.604		
.20	.616		
.30	.592		

Hydrochloric acid (0.050 *N*) Magnesium chloride

C_{salt}, *N*	*k*	
0	0.497	0.497
0.097	.596	
.194	.621	
.291	.647	
.388	.647	0.611
.486	.596	

Perchloric acid (0.0516 *N*) Magnesium perchlorate

C_{salt}, *N*	*k*	
0	0.524	0.524
0.10	.597	
.20	.621	.621
.30	.597	
.40	.597	
.50	.572	

Pyridinium chloride (0.060 *N* + 0.040 *M* pyridine) Magnesium chloride

C_{salt}, *N*	*k*		
0	0.650	0.627	0.606
0.20	.669		
.40	.680		
.60	.659		

(0.030 *N* Pyridinium chloried +0.070 *M* Pyridine)

C_{salt}, *N*	*k*	
0	0.351	
0.20	.430	
.40	.430	0.410
.60	.390	

(1) There was no loss in weight in solutions of benzoic acid containing sodium benzoate, and the cylinder acquired a visible white film. With hydrogen peroxide present hydrogen evolution was partly suppressed, the rate was somewhat increased in the acid alone and was normal in acid +0.2 *N* benzoate, but fell off in the presence of more concentrated sodium benzoate.

(2) The same rate was found in sodium bisulfate and sulfuric acid solutions, within experimental error, and this is true in the presence of magnesium sulfate. The rate decreases as sulfate is added while in the other stronger acids the rate increases when salt is added. The cylinder ac-

quired a thin brown film, slowly in the acid or bisulfate solutions, more rapidly the more concentrated the magnesium sulfate.

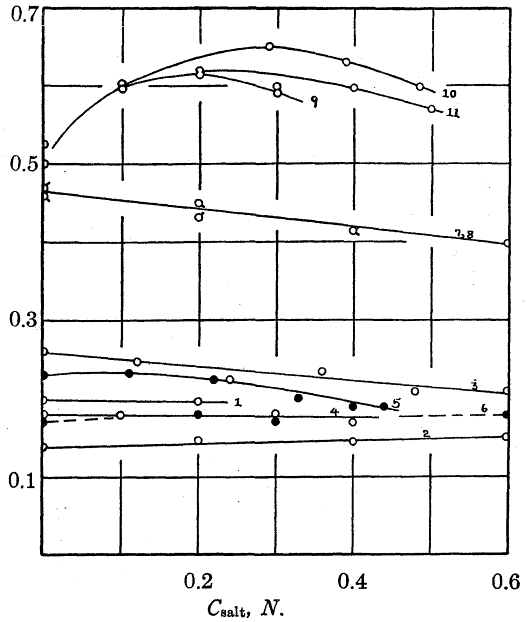

Fig. 2.—Dissolution rate constants *vs.* salt concentration. Acids: numbered as in Fig. 1.

(3) The rate in pyridinium chloride is higher than would be expected from the diffusion coefficient of Table I, but it decreases tremendously in the presence of excess pyridine. This was not known when the diffusion coefficients were measured, and it must be concluded that the measurements were not made under comparable conditions. This system is therefore omitted in further comparison.

(4) In every case except that of sulfuric acid and the bisulfate, the dissolution rates and diffusion coefficients change in the same direction on addition of salt. The magnitude of the change in dissolution rates is less than in diffusion coefficients, as would be expected from the diffusion theory; for even if pure acid is present initially, the magnesium salt is formed next the surface immediately.

Comparison of Diffusion and Dissolution Rates.—Values of D and k considered to be most nearly comparable were selected and are tabulated in Table III. The method of selection of most of the values is obvious; if the diffusion coefficient and the rate constant reach a maximum or a plateau near the same salt concentration, these values were chosen. In the case of sulfuric acid and the bisulfate, it seemed better to take the rate constant for the pure acid, but the maximum diffusion coefficient in the presence of salt.

TABLE III

COMPARISON OF DIFFUSION COEFFICIENTS AND DISSOLUTION RATE CONSTANTS

Acid	$D \times 10^3$, cm.²/min.	k, cm./min.
Benzoic	0.65	0.20
Citric	.70	.15
Monochloroacetic	.70	.23
Acetic	.76	.18
Formic	.85	.22
Tartaric	.85	.18
Sodium bisulfate	2.10	.46
Sulfuric	2.10	.46
Benzenesulfonic	3.00	.61
Hydrochloric	3.30	.64
Perchloric	3.60	.62

Discussion

While the dissolution rates do not fall in exactly the same order as the diffusion coefficients, the general trend is striking. Part of the lack of uniformity among the weaker acids undoubtedly is due to the fact that acids having salts of low solubility give low dissolution rates because of film formation. We cannot, however, account for the discrepancies among chloroacetic, formic and acetic acids, nor among benzenesulfonic, hydrochloric and perchloric acids.

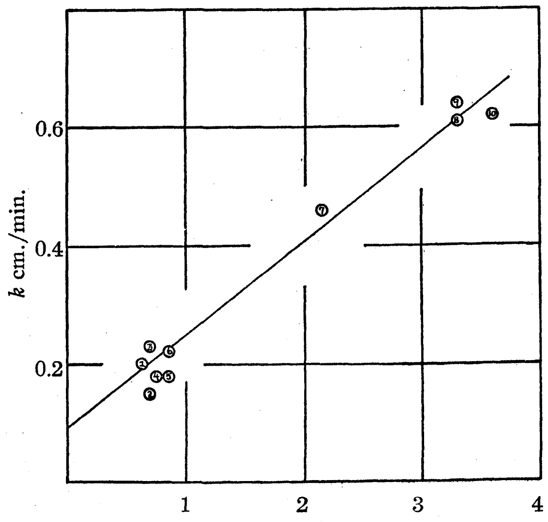

Fig. 3.—Dissolution rate constants *vs.* diffusion coefficients. Acids: 1, benzoic; 2, citric; 3, chloroacetic; 4, acetic; 5, tartaric; 6, formic; 7, sulfuric and bisulfate; 8, benzenesulfonic; 9, hydrochloric; 10, perchloric.

As shown in Fig. 3, the relation between k and D is reasonably well represented by a straight line which, however, does not pass through the origin. This type of relation was found before for dissolution rates in experiments with metal and other cylinders rotating at a higher speed in appropriate reagents.[2] Explanations of this extrapolation to a finite rate constant at zero diffusion coefficient are unsatisfactory, and as shown elsewhere[9] it is more probable that the true relation is of an exponential type

$$k = \alpha D^x$$

being nearly linear over the range of values plotted in Fig. 3. This exponential relation is consistent with a diffusion layer whose thickness increases with increasing diffusion coefficient, as is necessary from a consideration of turbulence in the solution near the metal surface.[2] Such a relation is also predicted from the expressions of Colburn[10] and Chilton and Colburn[11] derived to correlate heat and mass transfer in gas–liquid and gas–solid systems. The exponent x is given as $^2/_3$ by these authors.

From a log–log plot of k *vs.* D, the best value of x for these data is found to be approximately 0.70. In Fig. 4, values of k are plotted *vs.* $D^{0.70}$; the linear relation is at least as good as that of Fig. 3. The straight line is represented by the equation

$$k = 0.36D^{0.70}$$

A similar exponential relation holds for the data of ref. 2 and also of ref. 9. In the latter case, values for heat transfer are represented by the same equation as values for dissolution rates.

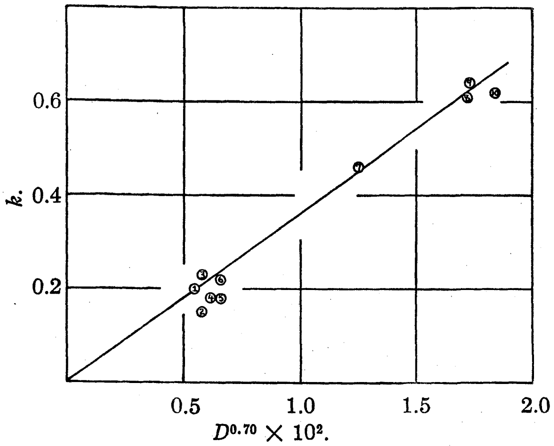

Fig. 4.—Dissolution rate constants *vs.* diffusion coefficients to the 0.70 power. Acids: numbered as in Fig. 3.

Summary

The diffusion coefficients of twelve acids have been measured in the porous glass disk type of diffusion cell, alone and in the presence of their magnesium salts when possible, otherwise with other salts present.

The dissolution rate of magnesium from cylinders rotating with a peripheral speed of 2000 cm./min. has been measured in the same acids in the presence of the same salts.

A comparison of diffusion coefficients and dissolution rate constants shows that they can be correlated fairly satisfactorily. The correlation is in agreement with a modification of the Nernst theory for such dissolution rates, and also with the Chilton–Colburn relations for heat and mass transfer at a phase boundary.

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[9] King and Howard, *Ind. Eng. Chem.*, **29**, 75 (1937).

[10] Colburn, *Trans. Am. Inst. Chem. Engrs.*, **29**, 174 (1933).

[11] Chilton and Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).

[CONTRIBUTION NO. 581 FROM THE KODAK RESEARCH LABORATORIES]

Studies in the Cyanine Dye Series. VII. New Dyes Containing Three Heterocyclic Nuclei

BY L. G. S. BROOKER AND L. A. SMITH

Cyanine dyes have been described in which a quinoline nucleus is linked through either the 2- or 4-position to a second heterocyclic nucleus. In the present paper, dyes of a new type are described in which a quinoline nucleus is linked through both of these positions to two other nuclei. These dyes differ from the previously known trinuclear dyes of the neocyanine type[1] since in the latter two nuclei are linked together by a three-carbon chain, the third nucleus forming part of a group attached to one of the carbon atoms of this chain.[2–5]

If 2,4-dimethylquinoline ethiodide (I) is treated with an excess of 2-iodoquinoline ethiodide in the presence of triethylamine, both methyl groups take part in the reaction, and a

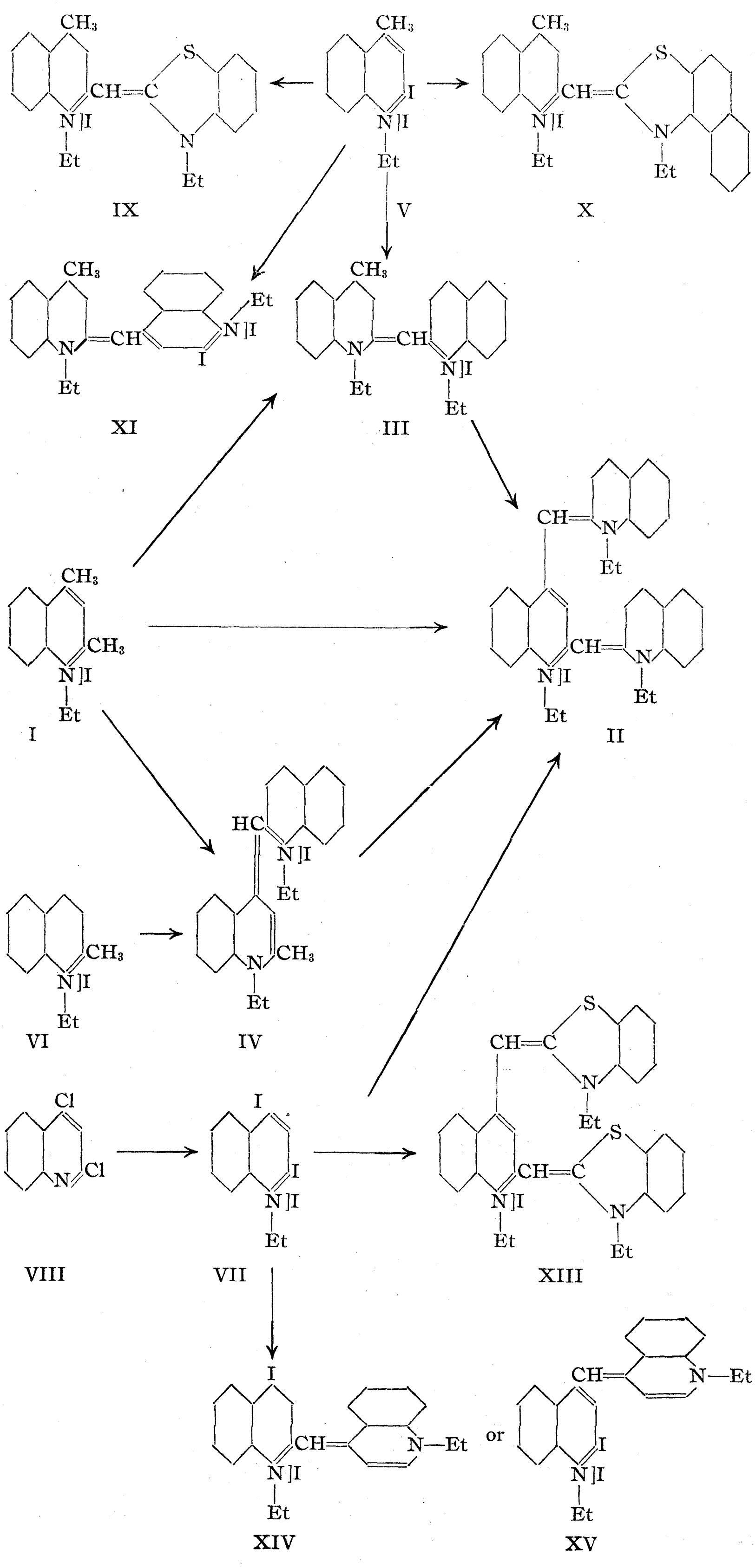
[1] Dundon, Schoen and Briggs, *J. Opt. Soc. Am.*, **12**, 397 (1926).

[2] Hamer, *J. Chem. Soc.*, 1472 (1928).

[3] Brooker, Hamer and Mees, *J. Opt. Soc. Am.*, **23**, 216 (1933).

[4] König, *Z. wiss. Phot.*, **34**, 15 (1935).

[5] Hamer, *J. Soc. Chem. Ind.*, **54**, 640 (1935).



new cyanine dye, 2,4-di-[(1-ethyl - 2(1) - quinolylidene) - methyl]-quinoline ethiodide (II) is formed. With equimolecular proportions of the two quaternary salts, however, a mixture of dyes is produced, the less soluble component of which, isolated as the perchlorate, was found to be identical with the perchlorate corresponding to 1,1′-diethyl-4-methyl-2,2′-cyanine iodide (III) made by condensing 2-iodolepidine ethiodide (V) with quinaldine ethiodide (VI). The second component of the mixture was not isolated in a pure state, but was without doubt the isomeric 1,1′-diethyl-2′-methyl-2,4′-cyanine iodide (IV). The absorption curve of the mixture of dyes was in complete agreement with this assumption, there being present distinct maxima corresponding to III and IV. The latter has been prepared by the action of potassium hydroxide on quinaldine ethiodide.[6]

It is reasonable to ascribe a certain reactivity to the methyl groups in III and IV and to regard these dyes as intermediate steps in the synthesis of II from I. This is substantiated by the fact that II was prepared from IV by interaction with a further proportion of 2-iodoquinoline ethiodide. In an attempted preparation of II from III, not enough of the desired dye was obtained for analysis, but there was sufficient to give the characteristically colored solution of II (see below).

A further preparation of II was carried out as follows:

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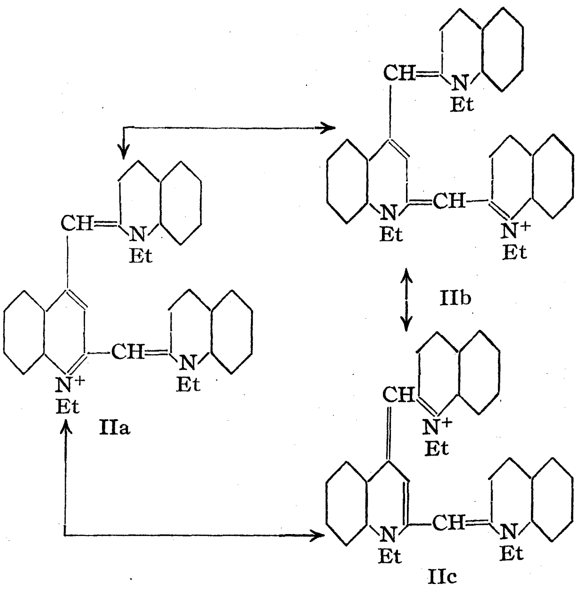
[6] Kaufmann and Vonderwahl, *Ber.*, **45**, 1413 (1912).

2,4-diiodoquinoline ethiodide (VII) was prepared from 2,4-dichloroquinoline (VIII) by heating the latter with an excess of ethyl iodide in a sealed tube at 100°. In VII the iodine atoms in positions 2 and 4 were both found to be reactive, since II was prepared by condensing it with VI, using triethylamine, it being best to use an excess of VI.

As obtained by any of the methods given, II consists of rather dark bronze crystals which dissolve in methyl alcohol to give a solution which is dull greenish-blue when sufficiently dilute but which develops a reddish color as the concentration is increased. The absorption curve of the dye (Fig. 1, A) is remarkable and differs in character from that ever previously described for a cyanine dye. There are two principal bands with maxima at 4800 and 6150 Å., respectively, that at the shorter wave length being narrower and somewhat stronger than the other. Between these bands there is a region of almost complete transmission with minimum absorption at about 5150 Å. In addition to the two principal bands, there is a weaker band with a distinct maximum at 4550 Å. The general appearance of the absorption curve is reminiscent of that of a mixture of two distinct cyanine dyes, the individual absorption curves of which overlap but very slightly.



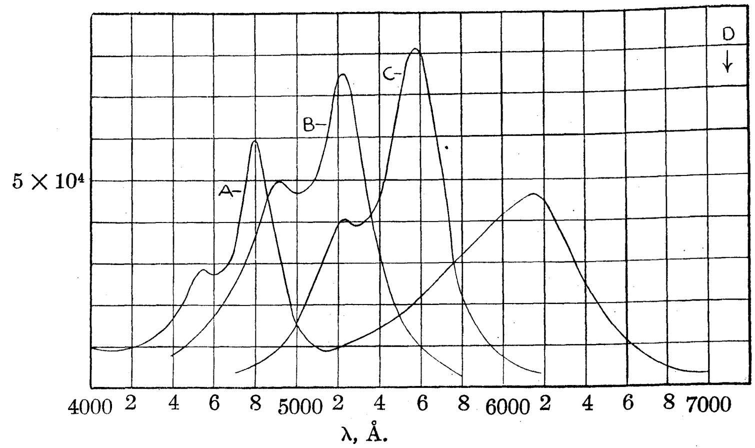
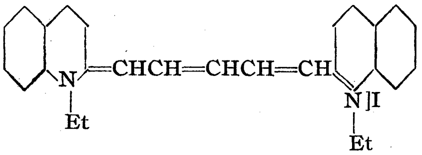


Fig. 1.—Absorption curves. A = 2,4-di[(1-ethyl-2(1)quinolylidene)methyl] quinoline ethiodide (II); B = 1,1′-diethyl-2,2′-cyanine iodide; C = 1,1′-diethyl-2,4′-cyanine iodide; D indicates maximum absorption of 1,1′-diethyl-2,2′-dicarbocyanine iodide (XII).

There is much direct and indirect evidence for the tautomerism of the cyanine dyes[7-9] and furthermore, it is plausible to assume that the color of these dyes is due to this tautomerism or, more precisely, to resonance within the conjugated chain (or chains) connecting the nitrogen atoms.[10] In the case of II this resonance may be represented as shown.

Now, the modes of resonance involved in IIa ↔ IIb and IIa ↔ IIc are those which are characteristic of 2,2′-cyanines and 2,4′-cyanines, respectively, while that of IIb ↔ IIc resembles that characteristic of 1,1′-diethyl-2,2′-dicarbocyanine iodide (XII),[11] but there is this difference, that whereas in XII the two nuclei are linked together by a simple pentamethenyl chain, in II a portion of the 5-carbon chain linking the two quinoline nuclei forms a part of the third quinoline nucleus.



XII

For purposes of comparison the absorption curves of 1,1′-diethyl-2,2′-cyanine iodide (Fig. 1, B) and of 1,1′-diethyl-2,4′-cyanine iodide (Fig. 1, C) are shown, these being the simple dyes the

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(7) Mills and Braunholtz, *J. Chem. Soc.*, **121**, 1489 (1922).

(8) Hamer, *ibid.*, 206 (1928).

(9) Brooker and Keyes, THIS JOURNAL, **57**, 2488 (1935).

(10) Compare Bury, *ibid.*, **57**, 2115 (1935).

(11) Fisher and Hamer, *Proc. Roy. Soc.* (London), **A154**, 703 1936).

characteristic linkages of which are simultaneously present in II. The absorption maximum of XII at 7080 Å., is indicated by the arrow (Fig. 1, D). The dye has a secondary maximum at 6510 Å.

It is reasonable to ascribe the unusual absorption of II to its unusual structure and specifically to the presence in the molecule of linkages characteristic of several distinct cyanine dye types. A point to be considered, however, is that whereas in a simple 2,2′-cyanine the conjugation between the two nitrogen atoms is complete in both the resonance formulas, in II the conjugation between the two nitrogen atoms of the 2,2′-cyanine linkage is interrupted in IIc. Similarly, the conjugation of the 2,4′-cyanine linkage is interrupted in IIb while the 2,2′-dicarbocyanine linkage is interrupted in IIa. Thus, although II contains conjugated linkages characteristic of three distinct cyanine dye types, in each of the three cases there is a further way of writing the formula of the dye in which the conjugation of these linkages is broken.

In the case of the meriquinoid dye Michler's Hydrol, it has been found that introducing a substituent (NH_2 or OH) in such a position that the molecule is no longer permanently quinonoid (giving Auramine or Michler's ketone, respectively) markedly lightens the color.[12] In the present case if it be assumed that that portion of the absorption curve of II which has its maximum at 6150 Å. is related to the modified dicarbocyanine system represented by IIb $\longleftrightarrow$ IIc, it follows that the effect of incorporating part of the polymethine chain of XII in a third quinoline nucleus, giving II, is to shift the absorption maximum 930 Å. toward the blue, and this marked hypsochromic effect may be due, in part at least, to the breaking of the conjugated dicarbocyanine system in IIa.

The relationship of the remainder of the absorption curve of II to the 3- and 5-carbon nitrogen–nitrogen linkages present in the dye remains obscure, although it is again noteworthy that the band at 4800 Å. lies at shorter wave length even than the absorption of the simple 2,2′-cyanine.

Two dyes closely related to II have also been prepared, these being 2,4-di-[(1-methyl-2(1)-quinolylidene)-methyl]-quinoline methiodide and 2,4-di-[(1-ethyl-2(1)-quinolylidene)-methyl]-quinoline methiodide. The absorption curves of these dyes are very similar to that of II, but the three differ considerably in their sensitizing action, that containing the three methyl groups being by far the strongest, although it is weaker than some of the cyanine dyes discovered in recent times. This dye sensitizes a bromide emulsion out to about 6700 Å. for a moderate exposure, with its maximum effect at 5550 Å., there being a weaker band with its head at about 6200 Å. The other two dyes sensitize over approximately the same range, but are weaker and show some desensitization.

It has long been known that IV is greatly inferior to 1,1′-diethyl-2,4′-cyanine iodide (Ethyl Red) as a sensitizer,[13] and Mills and Pope suggested that the presence of the substituent group in the chain of ethylenic linkages joining the two nitrogen atoms decreased the ability of the system to interact with light waves.[14] However, III is similarly greatly inferior as a sensitizer to 1,1′-diethyl-2,2′-cyanine iodide, although in this case the methyl substituent does not lie on the shortest chain connecting the two nitrogen atoms. That the depressant effect of a methyl group in the 4-(or 4-′)-position varies within wide limits, however, is demonstrated by the fact that 1′,2-diethyl-4′-methylthia-2′-cyanine iodide (IX), prepared from V, is inferior to 1′,2-diethylthia-2′-cyanine iodide to a much smaller extent, whilst 1′,2-diethyl-4′-methyl-3,4-benzothia-2′-cyanine iodide (X) is only very slightly weaker than the related unsubstituted dye.[15,16]

The absorption curves of the three dyes derived from 2-iodolepidine ethiodide were similar to those of the corresponding unsubstituted dyes, introduction of the 4′-methyl group either not affecting the position of the maximum (X) or else shifting it somewhat toward the blue (IX, 50 Å.) (III, 25 Å.).

The formation of a bluish-red impurity was observed in the preparation from V of III, IX and X, and was difficult to remove in the case of III. This impurity is doubtless due to the condensation of two molecules of V giving 1,1′-diethyl-2′-iodo-4-methyl-2,4′-cyanine iodide (XI) and a bluish-red dye, the composition of which corresponded to XI was obtained by the action of tri-

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[12] Watson, "Colour in Relation to Chemical Constitution," Longmans, Green and Co., New York, 1918, p. 108.

[13] Miethe and Book, *Ber.*, **37**, 2008 (1904).

[14] Mills and Pope, *Phot. J.*, **60**, 183 (1920).

[15] Hamer, *J. Chem. Soc.*, 2598 (1929).

[16] Brooker, U. S. Patents 1,861,836, 1,969,444.

ethylamine on V alone. The combined action of the two substituents in XI on the absorption is very slight, the maxima coinciding with those of the unsubstituted dye within the limits of error, but their effect on the sensitizing action is profound, XI giving no trace of a sensitizing band for ordinary exposures.

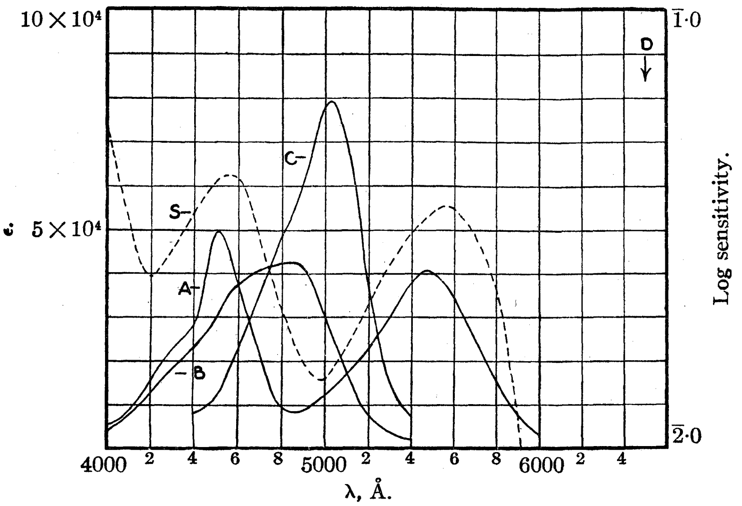
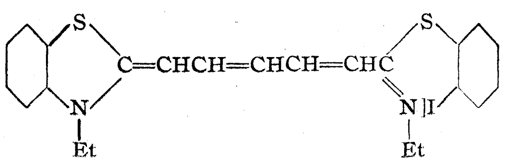


Fig. 2.—Absorption curves: A = 2,4-di[(2-ethyl-1(2)benzothiazolylidene)methyl]quinoline ethiodide (XIII); B = 1′,2-diethylthia-2′-cyanine iodide; C = 1′,2-diethylthia-4′-cyanine iodide; D indicates maximum absorption of 2,2′-diethylthiadicarbocyanine iodide (XVI). S = sensitizing curve of XIII in a chloride emulsion.

By the interaction of VII and 1-methylbenzothiazole ethiodide (in excess) using triethylamine, there was obtained 2,4-di-[(2-ethyl-1(2)-benzothiazolylidene)-methyl]-quinoline ethiodide (XIII). The dull reddish solution of this dye gives an absorption curve of the same general shape as that of II, the maxima being at 4515 and 5475 Å. and the minimum at 4875 Å. (Fig. 2, A). There is a further band at about 4300 Å., but it is ill defined.

The absorption curves of 1′,2-diethylthia-2′-cyanine iodide (Fig. 2, B) and 1′,2-diethylthia-4′-cyanine iodide (Fig. 2, C) are included for comparison, since the linkages characteristic of these dyes are simultaneously present in XIII. The third type of linkage present in XIII is a modification of that also present in 2,2′-diethylthiadicarbocyanine iodide (XVI), the absorption maximum of which is at 6500 Å.[11] (Fig. 2, arrow at D).



XVI

On the assumption already made, the effect of incorporating part of the polyene chain of XVI in a quinoline nucleus, giving XIII, is to move the maximum of absorption 1025 Å. nearer to the blue. It will also be noticed that the disposition of the B and C curves relative to the A curves is much the same in Figs. 1 and 2.

Dye XIII is a distinctly better photographic sensitizer than II. In a chloride emulsion there are two bands with maxima at about 4575 and 5575 Å., separated by a trough with its minimum at about 4975 Å. (Fig. 2, S). There is, in fact, a remarkably close resemblance between the absorption and sensitizing curves of XIII, and although similar cases have been noted since the earliest studies of the subject,[17,18] the present illustration is particularly striking on account of the unusual character of the curves. Compared with the absorption curve, the sensitizing curve appears to have been shifted bodily toward the red, but the extent of that shift is less than in many reported instances.[19]

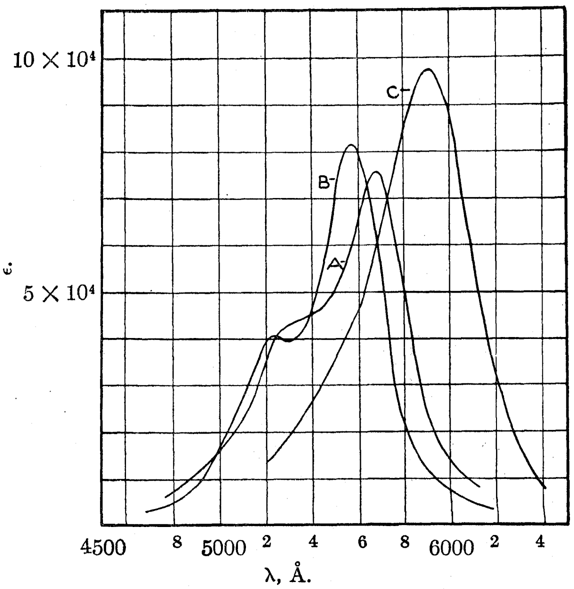


Fig. 3.—Absorption curves: A is 1,1′-diethyl-4-iodo-2,4′-cyanine iodide (XIV) or 1,1′-diethyl-2-iodo-4,4′-cyanine iodide (XV); B is 1,1′-diethyl-2,4′-cyanine iodide; C is 1,1′-diethyl-4,4′-cyanine iodide.

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(17) Vogel, *Ber.*, **6**, 1302 (1873).

(18) Becquerel, *Compt. rend.*, **79**, 185 (1874).

(19) Compare, for example, Bloch and Hamer, *Phot. J.*, **68**, 21 (1928); also Brooker and Keyes, THIS JOURNAL, **57**, 2492 (1935).

The dye similar to XIII but containing three methyl groups attached to the nitrogen atoms was also prepared. This was similar in its sensitizing action but somewhat stronger.

An attempt to prepare a dye containing three quinoline nuclei by condensing VII with two molecules of lepidine ethiodide was unsuccessful, the composition of a dye which was isolated corresponding to either 1,1′-diethyl-4-iodo-2,4′-cyanine iodide (XIV) or 1,1′-diethyl-2-iodo-4,4′-cyanine iodide (XV). The absorption curve of the dye (Fig. 3, A) has its maximum at 5675 Å. and accordingly XIV is considered to be the more likely formula since the strong hypsochromic effect that must be ascribed to the 2-iodine atom in XV, if this is held to be the correct formula, is at variance with the results observed in the case of XI, in which the 2′-iodine atom appears to counteract the, if anything, weakly hypsochromic effect of the 4-methyl group (compare III, IX and X). The sensitizing action of the dye resembles that of 1,1′-diethyl-2,4′-cyanine iodide more than it does that of 1,1′-diethyl-4,4′-cyanine iodide, but it is weaker than either of these. It gives an almost uniform extension of the spectrum to 6200 Å., with some desensitization.

The absorptions of the dyes were all determined for methyl alcoholic solutions and in the curves the molecular extinction coefficient, ϵ, is plotted against wave length. We are indebted to Dr. L. A. Jones and to Mr. E. E. Richardson for these results, to Dr. L. T. Hallett for the analyses, to Mr. G. Silberstein for the sensitizing curve, and to several other colleagues for the other photographic data.

Experimental

Intermediates

2,4-Dimethylquinoline Methiodide.[20]—The base (157 g.; 1 mol) was heated under reflux with methyl iodide (180 g.; 1.25 mols) for two days. The solid cake was ground with acetone and the yellow powder recrystallized from methyl alcohol (12 cc. per g.); yield of first crop 65%, increased to 93% by further crops. After a further recrystallization the pale yellow tables had m. p. 271–272°.

Anal. Calcd. for $C_{12}H_{14}IN$: I, 42.44. Found: I, 42.52.

2,4-Dimethylquinoline ethiodide (I)[20] was prepared similarly; yield 77% before and 73% after recrystallization (two crops). After a further recrystallization, the pale yellow crystals had m. p. 231–233°.

Anal. Calcd. for $C_{13}H_{16}IN$: I, 40.55. Found: I, 40.71.

2-Iodolepidine Ethiodide (V).—2-Chlorolepidine (50 g.; 1 mol) was heated under reflux with ethyl iodide (110 g.; 1.5 mols) for eight days in darkness.[8] The product was ground with acetone and weighed 64.6 g. (54%) and had m. p. 216–218° dec. After two recrystallizations from water (200 cc. per g.) (charcoal) the minute yellow crystals had m. p. 218–219° dec.

Anal. Calcd. for $C_{12}H_{13}I_2N$: I, 59.73. Found: I, 59.75.

2,4-Dihydroxyquinoline was made by the method of Ashley, Perkin and Robinson,[21] by treating methyl acetylanthranilate with sodium in toluene. These authors do not specify the time of heating nor do they give yields. We found that by refluxing for four hours the yield of purified product varied between 28 and 31%.

Anal. Calcd. for $C_9H_7NO_2$: C, 67.04; H, 4.38. Found: C, 67.38; H, 4.30.

2,4-Dichloroquinoline (VIII) was prepared from 2,4-dihydroxyquinoline by a modification of the method of Friedländer and Weinberg.[22] Contrary to the experience of Koller,[23] we were able to carry out the preparation satisfactorily using phosphorus pentachloride. In one experiment 2,4-dihydroxyquinoline (38.4 g.; 1 mol) was heated with phosphorus pentachloride (100 g.; 2 mols) and phosphorus oxychloride (80 cc.) at 100° for two hours. The excess of phosphorus oxychloride was removed under reduced pressure and the residue poured on ice. The solid was ground with ice water and filtered after neutralizing with sodium carbonate. It was then distilled *in vacuo;* yield 35 g. (74%). After recrystallization from methyl alcohol (2.5 cc. per g.) the yield (32.7 g.) was 69% (two crops). The colorless crystals melted at 66–67°.

Anal. Calcd. for $C_9H_5NCl_2$: C, 54.54; H, 2.55. Found: C, 54.39; H, 2.56.

2,4-Diiodoquinoline Methiodide.—2,4-Dichloroquinoline (4 g.; 1 mol) and methyl iodide (14.4 g.; 5 mols) were heated at 100° in a sealed tube for three days. The product was ground with acetone; yield 5.1 g. (49%). After two recrystallizations from nitromethane (1 liter per g.) the yellow crystals had m. p. 236–237°, dec.

Anal. Calcd. for $C_{10}H_8I_3N$: I, 72.80. Found: I, 72.45.

2,4-Diiodoquinoline ethiodide (VII) was prepared similarly by heating at 100° for three weeks; crude yield 47%. After one recrystallization from nitromethane (500 cc. per g.) the yellow crystals had m. p. 235–236°, dec.

Anal. Calcd. for $C_{11}H_{10}I_3N$: I, 70.91. Found: I, 70.80.

Dyes

In all cases methyl alcohol was used for recrystallizing the dyes.

1,1′-Diethyl-4-methyl-2,2′-cyanine Perchlorate (cf. III).—Quinaldine ethiodide (3 g.; 1 mol), 2-iodolepidine ethiodide (4.25 g.; 1 mol) and triethylamine 2.9 cc.; 2.1 mols) were refluxed with absolute ethyl alcohol (25 cc.) for twenty minutes. Dye separated (62% yield) and after two recrystallizations was converted into the

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[20] Compare Beyer, *J. prakt. Chem.*, ii, **33**, 406 (1886).

[21] Ashley, Perkin and Robinson, *J. Chem. Soc.*, 382 (1930).

[22] Friedländer and Weinberg, *Ber.*, **15**, 2679 (1882).

[23] Koller, *ibid.*, **60**, 1108 (1927).

perchlorate by treatment with potassium perchlorate and given two further recrystallizations (500 cc. per g.). The characteristic brownish spheroidal crystal aggregates had m. p. 279–280° dec. The maximum absorption of the dye is at 5200 Å. A well-marked secondary band has its maximum at 4900 Å.

Anal. Calcd. for $C_{24}H_{25}ClN_2O_4$: C, 65.33; H, 5.72. Found: C, 65.00; H, 5.48.

When 2,4-dimethylquinoline ethiodide (3.1 g.; 1 mol) and 2-iodoquinoline ethiodide (4.1 g.; 1 mol) were similarly condensed using triethylamine (2.9 cc.; 2.1 mols) the yield of the mixed dyes was 86%. The absorption curve of the product at this stage showed two maxima of nearly equal strength at 5200 and 5550 Å. with a weaker one at 4900 Å. The mixture was converted into the perchlorates and extracted with boiling methyl alcohol (250 cc.). This removed most of the purplish-red dye (2,4′-cyanine) and after three recrystallizations the residue was identical (appearance; mixed m. p.; absorption) with the specimen obtained above. Found: C, 65.34; H, 5.64.

1,1′-Diethyl-2′-methyl-2,4′-cyanine Iodide (IV).—The earlier method was modified. A boiling solution of quinaldine ethiodide (29.9 g.; 2 mols) in ethyl alcohol (150 cc.) was treated with powdered potassium hydroxide (3.1 g.; 1 mol) with constant shaking and the whole refluxed for twenty minutes; yield after washing 66%, being 31% after two recrystallizations (25 cc. per g.); m. p. 191–192°.

Anal. Calcd. for $C_{24}H_{25}IN_2$: I, 27.11. Found: I, 27.11.

This dye has its maximum absorption at 5550 Å. with a secondary maximum at about 5225 Å.

2,4-Di-[(1-ethyl-2(1)-quinolylidene)-methyl]-quinoline Ethiodide (II). (A) From 2,4-Dimethylquinoline Ethiodide.—This salt (3.1 g.; 1 mol), 2-iodoquinoline ethiodide (16.4 g.; 4 mols), triethylamine (8.7 cc.; 6.2 mols) and ethyl alcohol (40 cc.) were refluxed for forty minutes. Dye separated on cooling and was washed (acetone, then water). After three recrystallizations (140 cc. per g.) the yield was 0.15 g. (2%). The dye formed minute dull bronze crystals, m. p. 291–292°, dec.

Anal. Calcd. for $C_{35}H_{34}IN_3$: C, 67.39; H, 5.50; I, 20.36; N, 6.74. Found: C, 66.72; H, 5.41; I, 20.39; N, 6.84.

(B) From 2,4-Diiodoquinoline Ethiodide.—This salt (2.7 g.; 1 mol), quinaldine ethiodide (6 g.; 4 mols), triethylamine (4.32 cc.; 6.2 mols) and ethyl alcohol (50 cc.) were refluxed for forty minutes. Dye separated on chilling and after washing was extracted with boiling methyl alcohol (75 cc. × 2). The first extract contained much purplish-red dye and was rejected, but the second extract deposited moderately pure product; wt. 0.4 g. (13%). After a further recrystallization (6.5%) the dye was analytically pure. Found: I, 20.32.

(C) From 1,1′-Diethyl-2′-methyl-2,4′-cyanine Iodide (IV).—This dye (2.34 g.; 1 mol) and 2-iodoquinoline ethiodide (8.24 g.; 4 mols) were refluxed for forty minutes with ethyl alcohol (30 cc.) and triethylamine (4.2 cc.; 6.2 mols). The dye which separated was washed, extracted with hot methyl alcohol (15 cc.) and the residue twice recrystallized; yield 4.5%. Found: I, 20.35.

The specimens prepared by the three methods were identical (appearance; mixed m. p.; absorption; sensitizing).

2,4-Di-[(1-methyl-2(1)-quinolylidene)-methyl]-quinoline methiodide was prepared similarly, using method B (above). Some unused 2,4-diiodoquinoline methiodide was removed by filtration from the hot reaction mixture together with some dye which apparently consisted of 2,2′- and 2,4′-cyanine. The hot filtrate deposited the desired dye on cooling (15% yield). Dull brownish crystals from methyl alcohol (225 cc. per g.); yield 10%; m. p. above 310° dec., with shrinking from about 300°.

Anal. Calcd. for $C_{32}H_{28}IN_3$: C, 66.07; H, 4.86; I, 21.84; N, 7.23. Found: C, 65.40; H, 4.94; I, 21.64; N, 7.23.

This dye has absorption maxima at 4775 and 6050 Å. The third band is not so clearly defined in this case, but appears to be at about 4500 Å.

2,4-(Di-[(1-ethyl-2(1)-quinolylidene)-methyl]-quinoline methiodide was prepared using method A (above). Dye separated during the reaction and was filtered from the hot liquor and given three recrystallizations (700 cc. per g.); yield 6%. The minute crystals had a coppery luster; m. p. 302–303° dec.

Anal. Calcd. for $C_{34}H_{32}IN_3$: I, 20.83; N, 6.90. Found: I, 20.84; N, 7.09.

In a later experiment better results were obtained using *n*-propyl alcohol as solvent, and refluxing for forty minutes, the yields being 31% before and 15% after recrystallization. The absorption of this dye was like that of II.

2,4-Di-[(2-ethyl-1(2)-benzothiazolylidene)-methyl]-quinoline Ethiodide (XIII).—2,4-Diiodoquinoline ethiodide (1.34 g.; 1 mol), 1-methylbenzothiazole etho-*p*-toluenesulfonate (3.5 g.; 4 mols), triethylamine (2.15 cc.; 6.2 mols) and ethyl alcohol (50 cc.) were refluxed for forty minutes. Solid separated on cooling but this was not the dye sought for and was removed. Ether was added to the filtrate and the dye separated; yield 0.25 g. (15%). After two recrystallizations (50 cc. per g.) the yield was 3%. The minute brownish crystals with greenish reflex had m. p. 274–276° dec.

Anal. Calcd. for $C_{31}H_{30}IN_3S_2$: I, 19.97. Found: I, 19.88.

The sensitizing curve was determined on the monochromatic sensitometer described by Jones and Sandvik,[24] the sensitivity being the reciprocal of the exposure (in ergs/sq. cm.) necessary to produce a density of 1.0.

2,4-Di-[(2-methyl-1(2)-benzothiazolylidene)-methyl]-quinoline methiodide was prepared similarly. Dye separated in the hot reaction mixture; yield 33% (17% after two recrystallizations; 1200 cc. per g.). The dye formed a brown felt of minute crystals with a greenish reflex and had m. p. 301–302° dec.

Anal. Calcd. for $C_{28}H_{24}IN_3S_2$: I, 21.39. Found: I, 21.42.

1,1′-Diethyl-4-iodo-2,4′-cyanine Iodide (XIV), or 1,1′-Diethyl-2(or 2′)-iodo-4,4′-cyanine Iodide (XV).—Lepidine ethiodide (3 g.; 4 mols), 2,4-diiodoquinoline ethiodide (1.34 g.; 1 mol), ethyl alcohol (40 cc.) and triethylamine (2.15 cc.; 6.2 mols) were refluxed for forty minutes. Dye (0.7 g.) separated on cooling and was purified by several

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[24] Jones and Sandvik, *J. Opt. Soc. Am.*, **12**, 401 (1926).

recrystallizations (200 cc. per g.). The dye formed beautiful prisms with a greenish-bronze reflex; m. p. above 300°, dec., with sintering from 275°.

Anal. Calcd. for $C_{23}H_{22}I_2N_2$: I, 43.76. Found: I, 43.56.

1′,2 - Diethyl - 4′ - methylthia - 2′ - cyanine iodide (IX) was obtained from V in similar fashion to III, using 1-methylbenzothiazole etho-*p*-toluenesulfonate. The yield of crude product was 84%, and 45% after two recrystallizations (125 cc. per g.). The orange-yellow needles had m. p. 276–277.5°, dec.

Anal. Calcd. for $C_{22}H_{23}IN_2S$: I, 26.76. Found: I, 26.86.

The maximum absorption is at 4800 Å.

1′,2 - Diethyl - 4′- methyl - 3,4 - benzothia - 2′ - cyanine iodide (X) was obtained similarly using 2-methyl-β-naphthothiazole etho-*p*-toluenesulfonate. The yield of product was 57% before and 42% after recrystallization (325 cc. per g.). The minute reddish-orange needles had m. p. 272–274°, dec.

Anal. Calcd. for $C_{26}H_{25}IN_2S$: I, 24.21. Found: I, 24.19.

The dye has its maximum absorption at 5000 Å. There is an indefinite secondary band with its head at about 4800 Å.

1,1′ - Diethyl - 2′ - iodo - 4 - methyl - 2,4′ - cyanine Iodide (XI).—2-Iodolepidine ethiodide (4.25 g.; 2 mols), triethylamine (1.5 cc.; 2.1 mols) and ethyl alcohol (25 cc.) were refluxed for twenty minutes. Dye separated from the hot reaction mixture; yield 71% (44%; 140 cc. per g.). After a further recrystallization (yield 20%) the greenish-bronze crystals had m. p. 231–232°, dec.

Anal. Calcd. for $C_{24}H_{24}I_2N_2$: C, 48.49; H, 4.07; I, 42.73. Found: C, 48.65; H, 4.10; I, 42.37.

Summary

1. Both the methyl groups in 2,4-dimethylquinoline ethiodide can undergo condensation with 2-iodoquinoline ethiodide and there results a cyanine dye of a new type containing three quinoline nuclei. The same dye is formed when 2,4-diiodoquinoline ethiodide is condensed with quinaldine ethiodide and also when 1,1′-diethyl-2′-methyl-2,4′-cyanine iodide is condensed with 2-iodoquinoline ethiodide.

2. The absorption curve of the new dye is unusual. It consists of two distinct bands separated by a trough of almost complete transmission. This is probably due to the unusual structure of the dye, for the molecule contains linkages characteristic of three distinct cyanine dye types.

3. 2,4-Diiodoquinoline ethiodide condenses with 1-methylbenzothiazole etho-*p*-toluenesulfonate to give a trinuclear dye containing one quinoline and two benzothiazole nuclei. The absorption curve of this dye likewise consists of two distinct bands and bears a very close resemblance to the sensitizing curve of the dye for silver chloride, thus affording a particularly striking example of this relationship.

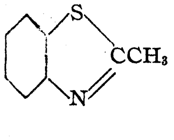
ROCHESTER, N. Y. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION NO. 582 FROM THE KODAK RESEARCH LABORATORIES]

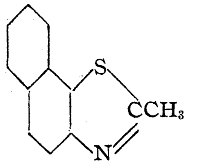
Studies in the Cyanine Dye Series. VIII. Dyes Derived from 2-Methylphenanthro-[9,10]-thiazole

BY G. H. KEYES AND L. G. S. BROOKER

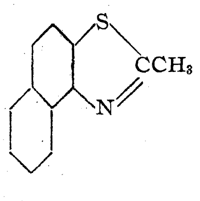
Certain cyanine dyes derived from 1-methylbenzothiazole (I) are well known, and in the search for effective photographic sensitizers, cyanines have been prepared from the methyl-α- and β-naphthothiazoles (II and III, respectively)[1,2,3] some of which dyes proved to be of considerable value. It was accordingly felt to be of interest to attempt to prepare dyes from 2-methylphenanthro-[9,10]-thiazole (IV), since this base may be considered to bear a similar relationship to II (or III) as III (or II) bears to I.



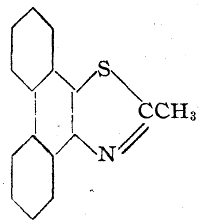
I



II



III



IV

The method used for preparing IV was a modi-

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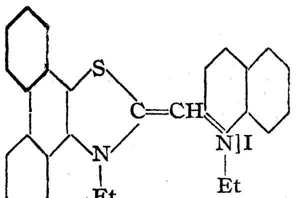
(1) Brooker, U. S. Patent 1,935,696; 1,969,444.

(2) Hamer, *J. Chem. Soc.*, 2598 (1929).

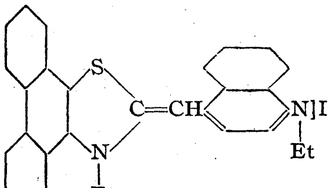
(3) Brooker and White, THIS JOURNAL, **57**, 547, 2480 (1935).

fication of that used by Jacobson[4] for the preparation of 2-methyl-β-naphthothiazole, 9-acetaminophenanthrene[5] being converted into the thioacetamino compound by treatment with phosphorus pentasulfide in hot dry toluene, and this being oxidized to the base by potassium ferricyanide in cold dilute alkaline solution. The pure base was obtained as nearly colorless needles with m. p. 145–147°, but the yield was only about 0.25%, calculated from the phenanthrene used as starting material.

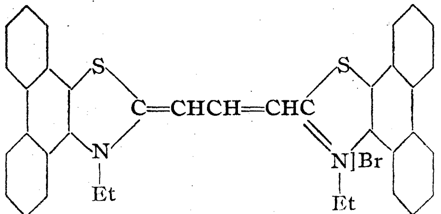
The metho- and etho-*p*-toluenesulfonates of the base were prepared by heating with the appropriate sulfonic esters, but the base reacted with these even more slowly than 2-methyl-β-naphthothiazole. Heating at high temperatures, too, had to be avoided on account of the tendency to decompose on the part of the esters, particularly the ethyl ester. From the appropriate *p*-toluenesulfonates the methiodide and ethiodide of the base were obtained and analyzed, but these salts were sparingly soluble and the *p*-toluenesulfonates themselves were chosen for submitting to certain dye condensations. From the etho-*p*-toluenesulfonate there was thus obtained 1′,2-diethyl-3,4,5,6-dibenzothia-2′-cyanine iodide (V), 1′,2-diethyl-3,4,5,6-dibenzothia-4′-cyanine iodide (VI) and 2,2′-diethyl-3,4,3′,4′,5,6,5′,6′-tetrabenzothiacarbocyanine bromide (VII) by condensation with 2-iodoquinoline ethiodide, quinoline ethiodide and ethyl orthoformate, respectively. In no case was the yield of dye high, and this is probably due in part to the presence in the ether-washed etho-*p*-toluenesulfonate employed of hydro-*p*-toluenesulfonate, formed by the union of the base with *p*-toluenesulfonic acid resulting from the decomposition of the sulfonic ester by elimination of ethylene.



V



VI



VII

It is interesting to compare dyes V, VI and VII with the related simpler dyes derived from I, II and III. In the thia-2′-cyanine series, the 1′,2-diethyl dyes derived from I, II and III are all known,[1,2] but in the present work the yields of those derived from II and III have been improved by the use of triethylamine.[6]

In the thia-4′-cyanine series, the dye derived from I, 1′,2-diethylthia-4′-cyanine iodide, was first described by Braunholtz and Mills[7] but we have obtained it in greatly increased yield by using excess of quinoline ethiodide and of potassium hydroxide in its preparation. High yields of the dyes from II and III were similarly obtained.

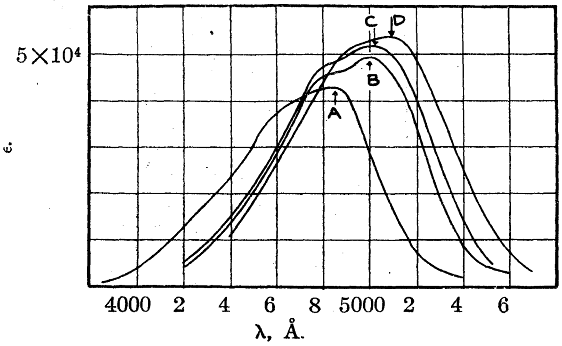


Fig. 1.—Absorption curves: A, 1′,2-diethylthia-2′-cyanine iodide; B, 1′,2-diethyl-5,6-benzothia-2′-cyanine iodide; C, 1′,2-diethyl-3,4-benzothia-2′-cyanine iodide; D, 1′,2-diethyl-3,4,5,6-dibenzothia-2′-cyanine iodide (V).

The absorption curves of the thia-2′-cyanines are given in Fig. 1, those of the thia-4′-cyanines in Fig. 2, and those of the thiacarbocyanines in Fig. 3. In all cases the molecular extinction coefficient, ε, is plotted against the wave length, λ, in Å. In all three series, A, B, C and D indicate the curves of the dyes derived from I, II, III and IV, respectively, and the maxima are indicated by arrows.

The wave lengths of maximum absorption of the

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[4] Jacobson, *Ber.*, **20**, 1897 (1887).

[5] Schmidt and Strobel, *ibid.*, **34**, 1461 (1901).

[6] Brooker and Keyes, THIS JOURNAL, **57**, 2488 (1935).

[7] Braunholtz and Mills, *J. Chem. Soc.*, **121**, 2004 (1922).

dyes are given in the table, the differences between adjacent values being given also.

Table of Absorption Maxima, in Å.

	A		B		C		D
Fig. 1	4850		5000		5025		5100
		150		25		75	
Fig. 2	5025		5215		5225		5300
		190		10		75	
Fig. 3	5575		5925		5950		6125
		350		25		175	

It has been shown previously that, in the thiacarbocyanine series, dyes derived from β-naphthothiazole have their maximum absorption nearer the red, in general, than the corresponding dyes derived from α-naphthothiazole,[3] and this rule is now seen to hold in the thia-2′-cyanine and thia-4′-cyanine series also.

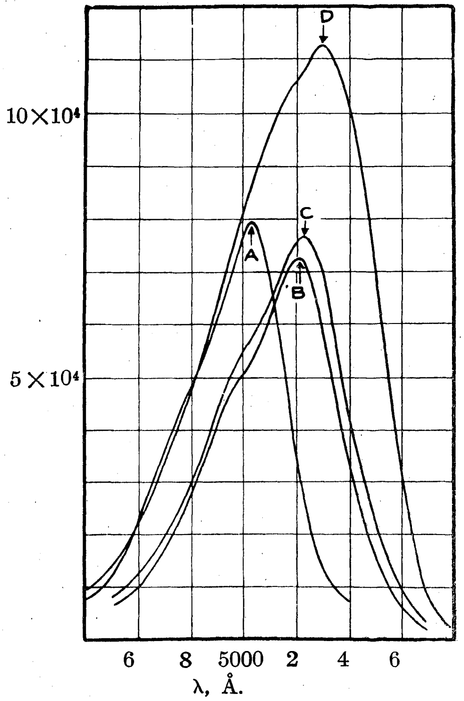

Fig. 2.—Absorption curves: A, 1′,2-diethylthia-4′-cyanine iodide; B, 2′,2-diethyl-5,6-benzothia-4′-cyanine iodide; C, 1′,2-diethyl-3,4-benzothia-4′-cyanine iodide; D, 1′,2-diethyl-3,4,5,6-dibenzothia-4′-cyanine iodide (VI).

A second generalization is that in every case a dye containing the phenanthro-[9,10]-thiazole nucleus has its absorption band nearer the red end of the spectrum than either of the corresponding dyes derived from a naphthothiazole. It is worthy of notice, however, that the shift produced when the benzothiazole nucleus (or nuclei) of a dye is replaced by α-naphthothiazole is at least twice as great as that produced when the β-naphthothiazole nucleus (or nuclei) of the dye in the same series is replaced by phenanthro-[9,10]-thiazole, although in both these processes the lighter nuclei of the two pairs have been weighted in the same way.

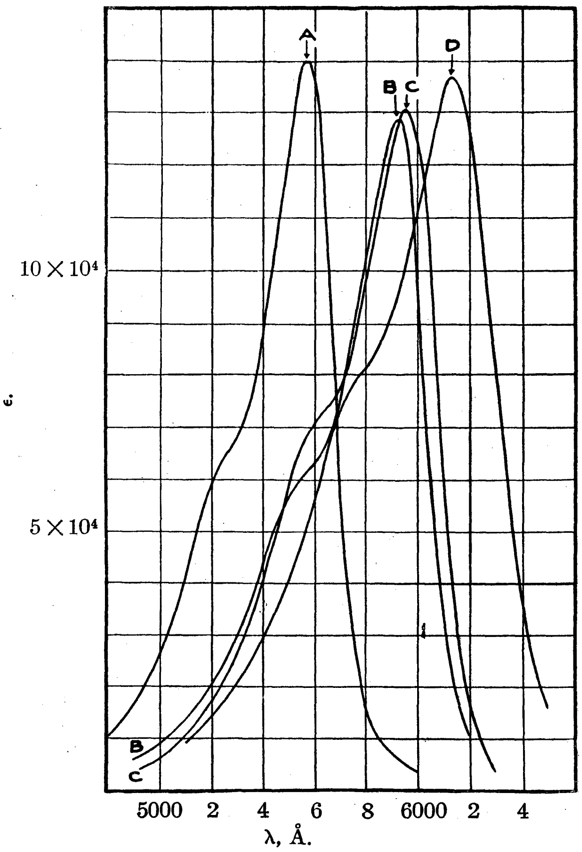

Fig. 3.—Absorption curves: A, 2,2′-diethylthiacarbocyanine iodide; B, 2,2′-diethyl-5,6,5′,6′-dibenzothiacarbocyanine bromide; C, 2,2′-diethyl-3,4,3′,4′-dibenzothiacarbocyanine bromide; D, 2,2′-diethyl-3,4,3′,4′,5,6,5′,6′-tetrabenzothiacarbocyanine bromide (VII).

Within each series the curves show a very marked resemblance to one another. Thus the four curves in Fig. 1 are all of the same general shape, there being in each case a principal band with a pronounced secondary band nearer the region of shorter wave length. The maximum values for ε lie very close together, also, and the same holds true, with one exception, for the curves in the other two figures. In Fig. 2 there is again a secondary band nearer the blue in each case, and curves A, B and C have maximum values of ε which are close together, but the value for D is considerably higher. The maximum value of ε for a thia-4′-cyanine is markedly higher than for the corresponding thia-2′-cyanine, and is highest of all for the corresponding thiacarbocyanine (Fig. 3). The curves in Fig. 3 have sharp maxima and there are again secondary bands nearer the blue.

The dyes were tested photographically after incorporation in a bromide emulsion. In the thia-2′-cyanine series (as in the thiacarbocyanine series[3]) the β-naphthothiazole derivative was a stronger sensitizer than the α-derivative but V is weaker than either of these. The thia-4′-cyanines which are derivatives of II and III are sensitizers for the green portion of the spectrum[8] with maxima at about 5400 Å., and each gives a second, less well-defined maximum nearer the blue. Here again the β-naphthothiazole derivative is the stronger sensitizer of the two. Dye VI sensitizes to about 6400 Å. for a moderate exposure, but the band is very flat and it is difficult to find a maximum.

The sensitizing action of the thiacarbocyanine dyes derived from II and III has already been described.[2,3] The dye VII is a relatively poor sensitizer. Its action extends to 6900 Å., but there is a decided gap between the regions of ordinary and of extra-sensitivity. The maximum effect is at 6550 Å., but even at this wave length VII is markedly inferior to either of the 2,2′-diethylthiacarbocyanines derived from the methyl naphthothiazoles, although their sensitizing maxima lie nearer to the blue.

We again wish to thank Dr. L. A. Jones and Mr. E. E. Richardson for the absorptions (which were all determined for methyl alcoholic solutions) and Dr. L. T. Hallett for the analyses except those marked by an asterisk which were kindly provided by Dr. S. F. Darling.

Experimental

9-Nitrophenanthrene, m. p. constant at 112.5–114.5°, was prepared by the method of Schmidt and Heinle[9] who give m. p. 116–117°. The yield of pure product was 4.5%.

9-Aminophenanthrene, m. p. 132–133°, was obtained in a yield of 27% using Schmidt and Strobel's method.[5] These authors claim a yield of 93–99% of product with m. p. 135–136°. They also state that the base darkens in air, but we find it to be quite stable when pure.

Anal. Calcd. for $C_{14}H_{11}N$: C, 87.00; H, 5.74; N, 7.25. Found: C, 86.75*; H, 5.45*; N, 7.24.

9-Acetaminophenanthrene was obtained by the following modification of Schmidt and Strobel's method, which avoids using a large excess of acetic anhydride. The 9-amino compound (4.8 g.; 1 mol) was dissolved in glacial acetic acid (60 cc.), heated on a steam-bath, acetic anhydride (3 g.; 1.2 mols) added, and the whole heated at 100° for forty-five minutes. The product separated on cooling (5 g.; 86%) and was a nearly colorless crystalline powder with m. p. 204–208° which was sufficiently pure for the next stage. On recrystallization from methyl alcohol (75 cc. per g.) the m. p. was raised to 213–215° (Schmidt and Strobel give m. p. 207–208° with sintering from 205°).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.66; H, 5.57; N, 5.96. Found: C, 81.5*; H, 5.6*; N, 6.02.

9-Thioacetaminophenanthrene.—Jacobson[4] prepared thioacetyl-α-naphthylamine by fusing acetyl-α-naphthylamine with phosphorus pentasulfide. Hantzsch[10] improved on Hofmann's similar method for the preparation of thioacetamide[11] by using benzene in the reaction and in the following we used toluene.

9-Acetaminophenanthrene (5 g.; 1 mol) was dissolved in gently refluxing dry toluene (300 cc.), pyridine (1 cc.) was added (this improved the yield markedly) followed by finely powdered phosphorus pentasulfide (4.7 g.; 1 mol) with good mechanical stirring. Heating and stirring were continued for two hours, and the toluene was decanted from the sticky residue and extracted with hot 5% caustic soda solution. The chilled extract was acidified carefully with acetic acid and the thioacetyl compound separated as a brownish solid. This was redissolved in alkali and reprecipitated in the cold. (The moist product at this stage was sufficiently pure for conversion to IV.) After drying the yield was 61%. It was recrystallized from methyl alcohol (charcoal) (yield 20%) and formed buff-colored crystals with m. p. 181–182°, dec., not raised by further recrystallization.

Anal. Calcd. for $C_{16}H_{13}NS$: C, 76.45; H, 5.22; N, 5.58. Found: C, 76.4*; H, 5.1*; N, 5.56.

2-Methylphenanthro-[9,10]-thiazole.—A run of crude 9-thioacetaminophenanthrene was dissolved in dilute caustic soda and the solution chilled and aqueous potassium ferricyanide added until an excess was present as indicated by a permanent yellow color. The base which separated as a solid was extracted with ether, the extract dried over anhydrous potassium carbonate and the solvent removed; yield 53%, calculated from the acetyl compound. The base was recrystallized from methyl alcohol (yield 29%).

Anal. Calcd. for $C_{16}H_{11}NS$: C, 77.05; H, 4.45; N, 5.62. Found: C, 77.0*; H, 4.6*; N, 5.59.

2-Methylphenanthro-[9,10]-thiazole Methiodide.—The base (0.5 g.; 1 mol) and methyl *p*-toluenesulfonate (0.37 g.; 1 mol) were heated at 120–130° for one week. The solid product was dissolved in boiling methyl alcohol (30 cc.) and potassium iodide (0.66 g.; 2 mols) in water (10 cc.) was added to the filtered solution. The methiodide separated and was washed with acetone and dried; yield 0.4 g. (46%). The salt separated from methyl alcohol (25 cc.) as a nearly colorless crystalline powder with m. p. 206–208°, dec., after two further recrystallizations.

Anal. Calcd. for $C_{17}H_{14}INS$: I, 32.45. Found: I, 32.51.

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(8) Brooker, U. S. Patent 1,861,836; Brooker and Kodak Ltd., British Patent 378,445; Kodak-Pathé, French Patent 713,486.

(9) Schmidt and Heinle, *Ber.*, **44**, 1488 (1911).

(10) Hantzsch, *Ann.*, **250**, 264 (1888).

(11) Hofmann, *Ber.*, **11**, 340 (1878).

2-Methylphenanthro-[9,10]-thiazole Ethiodide.—Equimolecular proportions of base (1 g.) and ethyl *p*-toluenesulfonate (0.8 g.) were heated at 130–140° for ten days. A hot aqueous extract (40 cc.) of the solid product was treated with hot aqueous potassium iodide (1.4 g. in 10 cc.). The ethiodide was precipitated (0.4 g.; 24%) and was recrystallized from methyl alcohol (10 cc.; charcoal); yield 18.5%. The melting point, 202–204°, dec., of the cream-colored crystalline powder was unaltered after a second recrystallization.

Anal. Calcd. for $C_{18}H_{16}INS$: I, 31.32. Found: I, 30.86.

In the dye condensations the crude etho-*p*-toluenesulfonate of the base was washed with ether and then used without further purification.

1′,2-Diethyl-5,6-benzothia-2′-cyanine iodide was obtained in a yield of 86% before and 70% after recrystallization when triethylamine was used to effect the condensation. The corresponding yields given by Hamer,[2] who used potassium hydroxide, are 44 and 30%. We find that the m. p. is 287–289°, dec.

1′,2-Diethyl-3,4-benzothia-2′-cyanine iodide was obtained similarly in a yield of 70% before and 55% after recrystallization; Hamer gives 36 and 24%.

1′,2-Diethylthia-4′-cyanine iodide was obtained by the interaction of 1-methylbenzothiazole ethiodide (1 mol), quinoline ethiodide (1 mol) and sodium ethylate (1.2 mols) by Braunholtz and Mills[7] who obtained the pure dye in a yield of 9–13%. By using potassium hydroxide (1 mol) for the condensation our yields were 19.5% before and 15.5% after recrystallization from methyl alcohol (55 cc. per g.). Kaufmann and Vonderwahl[12] have shown that in a very similar preparation, that of Ethyl Red (1,1′-diethyl-2,4′-cyanine iodide), the yield of dye was much improved by using 100% excess of quinoline ethiodide. In the present case, use of 2 mols of quinoline ethiodide resulted in the yield of pure dye being raised to 19%, but by using 2 mols of potassium hydroxide also, the much more marked increase of yield to 59% was obtained. Use of 3 mols of quinoline ethiodide and of potassium hydroxide gave a yield of 63% of pure dye, the yield being calculated in all cases from the 1-methylbenzothiazole ethiodide.

1′,2-Diethyl-5,6-benzothia-4′-cyanine iodide was obtained similarly from 1-methyl-α-naphthothiazole etho-*p*-toluenesulfonate (1 mol) using 100% excess of quinoline ethiodide and of potassium hydroxide; yield 51% before and 45% after recrystallization from methyl alcohol (350 cc. per g.). After a further recrystallization (yield 39%) the scarlet needles had m. p. 285–288°, dec.

Anal. Calcd. for $C_{25}H_{23}IN_2S$: I, 24.87. Found: I, 24.76.

1′,2-Diethyl-3,4-benzothia-4′-cyanine iodide was obtained similarly, yield 33% before and 27% after recrystallization. After two further recrystallizations (yield 21%) from methyl alcohol (175 cc. per g.) the dye formed beautiful reddish-brown needles (transmitted light) with a metallic green reflex; m. p. 248–250°, dec.

Anal. Calcd. for $C_{25}H_{23}IN_2S$: I, 24.87. Found: I, 24.76.

1′,2 - Diethyl - 3,4,5,6 - dibenzothia - 2′ - cyanine Iodide (V).—2 - Methylphenanthro - [9,10] - thiazole etho-*p*-toluenesulfonate (0.9 g.; 1 mol) was condensed with 2-iodoquinoline ethiodide (0.82 g.; 1 mol) in absolute ethyl alcohol (30 cc.) using triethylamine (0.4 g.; 2 mols), the mixture being refluxed for one-half hour; yield 0.15 g. (13%) and 0.09 g. (8%) after recrystallization from methyl alcohol (180 cc.). The dull-red crystals had m. p. 248–250°, dec.

Anal. Calcd. for $C_{29}H_{25}IN_2S$: I, 22.66. Found: I, 22.28.

1′ - Ethyl - 2 - methyl - 3,4,5,6 - dibenzothia - 2′ - cyanine iodide was prepared similarly; yield 45% before and 18% after recrystallization from methyl alcohol (1800 cc. per g.). The bright red crystalline powder had m. p. 244–246°, dec.

Anal. Calcd. for $C_{28}H_{23}IN_2S$: I, 23.24. Found: I, 22.91.

The absorption of this dye resembles that of V, but the maximum lies at 5050 Å.

1′,2 - Diethyl - 3,4,5,6 - dibenzothia - 4′ - cyanine Iodide (VI).—2 - Methylphenanthro - [9,10] - thiazole etho - *p* - toluenesulfonate (1.1 g.; 1 mol) was condensed with quinoline ethiodide (0.7 g.; 1 mol) in absolute ethyl alcohol (25 cc.) using potassium hydroxide (0.14 g.; 1 mol) and refluxing for forty-five minutes; yield 10% before and 7% after recrystallization from methyl alcohol (1130 cc. per g.). The dull reddish-brown crystals had m. p. 244–247°, dec.

Anal. Calcd. for $C_{29}H_{25}IN_2S$: I, 22.66. Found: I, 22.43.

This reaction was carried out before the advantage of using excess of quinoline ethiodide and potassium hydroxide in thia-4′-cyanine condensations was discovered, but the experiment was not repeated owing to lack of material.

2,2′ - Diethyl - 3,4,3′,4′,5,6,5′,6′ - tetrabenzothiacarbocyanine Bromide (VII).—2-Methylphenanthro-[9,10]-thiazole etho-*p*-toluenesulfonate (1.75 g.; 2 mols) was refluxed with pyridine (25 cc.) and ethyl orthoformate (1.2 g.; 2 mols) for forty-five minutes. The dye was precipitated as the bromide; yield 0.077 g. (6%). After recrystallization from dichloroethylene (Soxhlet) the yield was 4%. The minute dark bronze crystals had m. p. 200–202°, dec.

Anal. Calcd. for $C_{37}H_{29}BrN_2S_2$: C, 68.80; H, 4.53. Found: C, 68.97; H, 4.34.

Summary

1. Weighting the benzothiazole nucleus with a fused-on benzene residue gives α- or β-naphthothiazole nuclei, and these are present in photographic sensitizers of value. Repetition of the weighting process leads to the phenanthro-[9,10]-thiazole nucleus, and dyes containing this nucleus have been prepared in the hope that they would also be effective sensitizers.

2. 2-Methylphenanthro-[9,10]-thiazole has

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[12] Kaufmann and Vonderwahl, *Ber.*, **45**, 1413 (1912).

been synthesized and from it the corresponding 1′,2-diethylthia-2′- and -4′-cyanine iodides and the 2,2′-diethylthiacarbocyanine bromide.

3. In no case was a dye derived from the new base a powerful sensitizer. The thiacarbocyanine, for example, was considerably inferior even at the wave length at which it conferred maximum sensitivity, to the corresponding dyes derived from the methyl-α- and β-naphthothiazoles.

4. In every case the dyes derived from 2-methylphenanthro-[9,10]-thiazole absorb nearer the red than the corresponding dyes derived from the methylnaphthothiazoles.

ROCHESTER, N. Y. RECEIVED OCTOBER 5, 1936

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

Carbonyl Sulfide. The Heat Capacity, Vapor Pressure, and Heats of Fusion and Vaporization. The Third Law of Thermodynamics and Orientation Equilibrium in the Solid

BY J. D. KEMP AND W. F. GIAUQUE

At the present time the most important problem in connection with the third law of thermodynamics relates to the circumstances under which false equilibrium complicates the practical application of this law. When either the third or the second law of thermodynamics is combined with experimental data to permit the evaluation of some desired quantity, it is implied that the observations were made under conditions of true equilibrium with respect to all processes under consideration.

Recent low temperature investigations have shown that lack of equilibrium exists in the cases of hydrogen, water and their deuterium analogs, carbon monoxide, nitric and nitrous oxides. For each of the above substances the entropy may be accurately calculated from spectroscopic data and it has been possible to give a satisfactory quantitative explanation of the discrepancy between the calorimetric and the spectroscopic values. Carbon monoxide, nitrous oxide (NNO) and nitric oxide (N_2O_2) enter the crystalline state without discrimination between the molecular orientation positions of carbon, nitrogen or oxygen in the crystal lattice. These neighboring atoms in the periodic system are very similar in size and it seems desirable to carry out experiments in which the possibility of lack of discrimination is investigated with more dissimilar atoms.

Linear, unsymmetrical, polyatomic molecules offer a particularly simple case since it is evident that only the two positions corresponding to a rotation of 180° are possible within a crystal lattice. The substance selected for investigation was the linear molecule, carbonyl sulfide (SCO). The measurements to be presented show that the practical application of the third law gives the correct entropy. However, thermal equilibrium was obtained with great difficulty in a considerable region below the melting point, as might be expected if the molecules were beginning to acquire random orientation in the equilibrium state at these temperatures.

Carbonyl Sulfide.—Carbonyl sulfide was made by dropping C. P. concentrated sulfuric acid into a saturated water solution of C. P. potassium sulfocyanate. All solutions were boiled and the preparation line was evacuated with a mercury diffusion pump to eliminate air. The gas was bubbled through a 33% sodium hydroxide solution and collected in a bulb cooled by liquid air. The last traces of water were removed by passing the gas through a tower containing phosphorus pentoxide. Generous first and last fractions were discarded, leaving about 425 cc. of liquid carbonyl sulfide. The gas was then bubbled through some of its own liquid for further purification, a procedure similar to that employed by Gray[1] and by Johnston and Giauque.[2] The final purification was effected by the use of a vacuum jacketed fractionating column; 135 cc. of purified liquid carbonyl sulfide remained after these treatments.

By means of the premelting effects which are superimposed on the heat capacity just below the melting point, it was possible to estimate that the final preparation contained less than one part in twenty thousand of liquid-soluble solid-insoluble impurity.

Apparatus.—A vacuum calorimeter assembly similar to that described by Giauque and Wiebe[3] was used for the measurements. A full description of a similar calorimeter has been given by Giauque and Egan.[4] The calorimeter, which has been given the laboratory designation Gold Calorimeter IV, weighed 443 g. It was 4 cm. in

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[1] Gray, *J. Chem. Soc.*, **87**, 1601 (1905).

[2] Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

[3] Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

[4] Giauque and Egan, *J. Chem. Phys.*, January (1937).

diameter and 12.5 cm. in length. In order to assure rapid distribution of thermal energy twelve radial vanes of gold, 0.2 mm. in thickness, were welded lengthwise to the inside wall of the calorimeter. The walls of the calorimeter were 1 mm. thick. A platinum inlet tube 2 cm. long and 2 mm. in diameter was welded to the top of the calorimeter and connected to a soda glass tube by means of a cobalt glass seal. Double silk covered, B. and S. gage No. 40, gold wire was wound on the calorimeter to serve as a thermometer heater; 0.175% of silver was added to the gold to increase the heater resistance at low temperatures. Other details of apparatus and procedure including the calibration of the standard thermocouples are given by Giauque and Egan.[4]

A copper-constantan thermocouple, of laboratory designation W-21, was wound around the calorimeter and one junction soldered into the platinum thermocouple well with Wood's metal. Thermocouple W-21 previously had been compared with thermocouple W-22, the present laboratory standard, which was calibrated against the laboratory helium gas thermometer. As the calorimeter could be used as a vapor pressure thermometer, comparisons of W-21 were made against oxygen and hydrogen vapor pressures. The calibration was found to agree within 0.05 degree. Below 20°K. the resistance thermometer was calibrated directly in terms of the vapor pressure of hydrogen. In conformity with other investigations carried out in this Laboratory, 0°C. was taken as 273.10°K.

Vapor Pressure.—As the calorimeter is well suited to maintaining a constant temperature for long periods of time, it was convenient to measure the vapor pressure of the carbonyl sulfide using a large diameter manometer which was connected to the calorimeter for that purpose. A Société Génevoise cathetometer with a precision of 0.002 cm. was used to compare the mercury levels with a standard meter hanging beside the manometer. The pressures were corrected to International centimeters of mercury, using data from the "I. C. T." for all the corrections with the exception of the meniscus height corrections which were taken from the work of Cawood and Patterson.[5] The standard acceleration of gravity was taken as 980.665 cm./sec.^{2} Sternwarte[6] has given 979.973 cm. sec.^{2} as the acceleration of gravity for this location.

The observations on the vapor pressure of liquid carbonyl sulfide have been represented by the following equation for the temperature region between 161.8 and 223.8°K.:

$$\log_{10} P(\text{int. cm. Hg}) = -(1318.260/T) + 10.15309 - 0.0147784T + 0.000018838T^2 \qquad (1)$$

The results are summarized in Table I.

TABLE I

VAPOR PRESSURE OF CARBONYL SULFIDE

Boiling point, 222.87°K.; 0°C. = 273.10°K.

T, °K.	$P_{\text{obs.}}$ Int. cm. Hg	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$T_{\text{obsd.}} - T_{\text{calcd.}}$
161.797	1.282	+0.001	−0.009
161.809	1.283	+ .001	− .005
166.097	1.913	+ .001	− .006
170.560	2.826	− .002	+ .009
175.404	4.219	+ .003	− .009
180.073	6.055	+ .001	− 002
185.100	8.733	.000	.000
190.205	12.388	+ .001	− .002
195.714	17.652	+ .004	− .004
201.401	24.851	− .001	+ .001
211.832	44.134	+ .005	− .002
216.628	56.266	− .010	+ .005
220.522	67.969	.000	.000
223.791	79.189	− .002	.000

The calculated pressure differences given in column three were obtained by assuming the temperature observations to be correct. In column four, the calculated temperature differences were obtained by assuming the observed pressures to be correct. Although the absolute values of the temperatures may be in error by several hundredths of a degree, the observed temperatures are given to 0.001° because of the high relative accuracy.

Melting Point.—The melting point was observed as a function of the percentage melted. Table II gives the results of these observations.

TABLE II

MELTING POINT OF CARBONYL SULFIDE

0°C. = 273.10°K.

Date and time	% Melted	T, °K. resistance thermometer	T, °K. thermocouple
12/2/35 11:10 A.M.	Heated into melting point		
1:05 P.M.	10	134.283	134.29
4:25 P.M.	10	134.275	134.27
5:05 P.M.	Supplied heat		
12/3/35 10:30 A.M.	25	134.298	134.29
1:30 P.M.	25	134.295	134.30
2:00 P.M.	Supplied heat		
5:35 P.M.	50	134.304	134.31
12/4/35 11:00 A.M.	50	134.303	134.30
		Accepted value	134.31 ± 0.05

In obtaining the accepted value, it was recognized that the small amount of impurity present caused an appreciable melting point lowering.

Table III contains a comparison of the melting and boiling points obtained in this research with those obtained by other observers.

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF CARBONYL SULFIDE

0°C. = 273.10°K.

Melting point, °K.	Boiling point, °K.	Observer
....	225.6	Hempel[7] (1901)
134.9	222.9	A. Stock and Kuss[8] (1917)
134.31 ± 0.05	222.87 ± 0.05	This research

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(5) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 522 (1933).

(6) Sternwarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

(7) Hempel, *Z. angew. Chem.*, **14**, 865 (1901).

(8) A. Stock and Kuss, *Ber.*, **50**, 159 (1917).

Measurement of the Amount of Carbonyl Sulfide.—The method of measuring the amount of carbonyl sulfide depended upon the fact that carbonyl sulfide is soluble in ethyl alcohol. By using liquid air, it was possible to condense the carbonyl sulfide in an ordinary glass bulb containing enough alcohol to lower the pressure of the carbonyl sulfide to about 2.5 atmospheres when it was warmed to room temperature. A bulb containing about 140 cc. of alcohol sufficed for weighing about 13.5 g. of carbonyl sulfide. Each bulb was fitted with a stopcock and one end of an interchangeable ground glass joint. A constriction was made in the stem of each bulb so that it could be sealed by fusing the glass, as it was considered unwise to subject the stopcocks to the pressure which was developed when the carbonyl sulfide was warmed to room temperature.

In order to measure heats of vaporization at a constant pressure, the gas was allowed to vaporize into a carefully calibrated five-liter bulb which was connected to a manometer and a constant pressure regulating device which has been described by Giauque and Johnston.[9] The five-liter bulb was thermostated at 25.00°C. The pressures were measured with the Société Génévoise cathetometer used as a comparison instrument in connection with a standard meter. The line volume outside of the thermostat was carefully determined and only amounted to 165 cc.

The procedure in determining the amount of carbonyl sulfide was as follows. After filling the large measuring bulb, the carbonyl sulfide was condensed in a weighed, evacuated bulb immersed in liquid air. The bulb was then taken off the line and its stem fused at the constriction. Although it was not necessary to use the measuring bulb after completing measurements of the heat of vaporization, its use was continued as a precaution against any accident which might have occurred to any of the weighing bulbs. Twelve weighing bulbs were required to complete the measurement of the amount of carbonyl sulfide.

The above procedure led incidentally to a value, 2.4849 ± 0.0005 g./l., of the density of carbonyl sulfide gas at 25°C. and one atmosphere. This value was derived from an average of eleven determinations at about one atmosphere.

The Heat Capacity of Carbonyl Sulfide.—The heat capacity measurements were made using the method fully described in previous papers from this Laboratory.[3,9] Calibrations of the resistance thermometer against thermocouple W-21 were taken simultaneously with the heat capacity measurements. From these data, a smooth table of resistance against temperature was constructed for use as a temperature scale for the heat capacity measurements. This procedure was followed because of the high precision of the resistance thermometer in measuring small temperature increments.

TABLE IV

HEAT CAPACITY OF CARBONYL SULFIDE

Molecular weight, 60.065; 2.534 moles in calorimeter. 0°C. = 273.10°K.

T, °K.	ΔT	C_p cal./deg./mole	Series
15.53	2.284	1.507	II
15.62	2.776	1.535	III
18.16	2.942	2.162	II
18.65	3.292	2.259	III
20.89	2.617	2.846	II
21.88	3.126	3.106	III
23.56	2.762	3.488	II
25.13	3.254	3.811	III
26.49	3.011	4.093	II
28.79	4.027	4.560	III
29.97	3.825	4.835	II
33.07	4.530	5.457	III
34.14	4.448	5.714	II
37.81	4.965	6.322	III
38.87	5.002	6.472	II
43.02	5.445	6.983	III
44.13	5.549	7.114	II
48.32	5.145	7.534	III
49.53	5.271	7.636	II
53.77	5.715	8.032	III
55.11	5.890	8.155	II
59.54	5.792	8.459	III
61.08	6.049	8.654	II
66.01	7.232	8.837	III
66.72	5.177	8.941	II
71.96	5.157	9.195	II
75.16	11.004	9.342	III
77.47	5.713	9.487	II
83.50	6.308	9.782	II
86.80	12.063	9.951	III
90.13	6.850	10.12	II
97.07	6.920	10.38	II
100.37	13.622	10.49	III
103.87	6.463	10.70	II
110.48	6.513	10.97	II
113.38	13.697	11.06	III
117.14	6.644	11.26	II
123.47	5.805	11.55	II
127.07	13.318	12.03[a]	III
128.04	3.250	11.81	II
131.07	2.647	12.38[a]	II
134.31	Melting point		
137.33	2.587	17.49	I
141.61	5.762	17.44	I
147.96	6.788	17.29	I
154.74	6.559	17.18	I
162.35	6.392	17.09	I
167.97	6.231	17.02	I
174.26	6.077	17.00	I
180.67	6.421	16.93	I
187.21	6.239	16.93	I
193.75	6.527	16.95	I
200.53	6.370	16.94	I
207.43	6.949	16.97	I
214.49	6.746	17.00	I
220.87	5.430	17.04	I
222.87	Boiling point		

[a] These points do not give the true heat capacity, but include some premelting.

The following constants were used in calculating the energy: 1.0004 absolute joules = 1 international joule, 4.185 absolute joules = 1 calorie. Table IV gives the observed heat capacities. Table V gives values of the heat capacities taken from the smooth curve. The data are shown graphically in Fig. 1.

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(9) Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

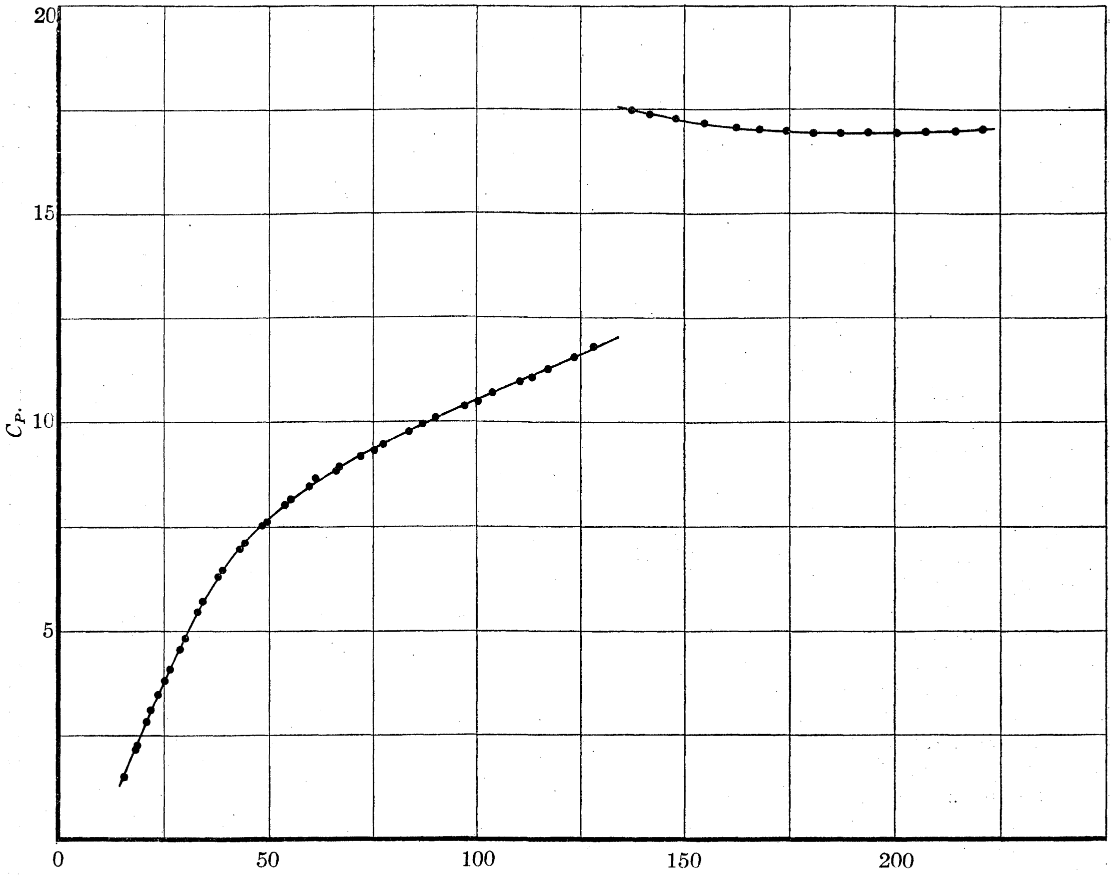

Fig. 1.—Molal heat capacity of carbonyl sulfide in calories per degree.

Table V

Heat Capacity of Carbonyl Sulfide

Molecular weight, 60.065

Values taken from smooth curve through observations

T, °K.	C_p cal./deg./mole.	T, °K.	C_p cal./deg./mole.
20	2.63	130	11.85
30	4.84	140	17.46
40	6.62	150	17.26
50	7.70	160	17.11
60	8.48	170	17.00
70	9.08	180	16.96
80	9.62	190	16.93
90	10.09	200	16.95
100	10.53	210	16.98
110	10.95	220	17.03
120	11.40		

Two series of heat capacity measurements were taken on solid carbonyl sulfide. For Series II, the carbonyl sulfide was cooled very slowly, forty-eight hours being required to complete solidification and another forty-eight hours to cool it to 60°K. In Series III, the carbonyl sulfide was cooled rapidly. It required about twelve minutes to complete solidification and about forty minutes more to cool it to 60°K. Further cooling to 15°K. required about two hours.

In both series, when 60°K. was approached in warming from 15°K., it became difficult to obtain thermal equilibrium due to some disturbance in the solid after the period of energy input. Normally, thermal equilibrium is obtained in the calorimeter in about five minutes after the period of energy input, but for the measurements from 60°K. to the melting point, 134.31°K., it required about an hour before thermal equilibrium was obtained.

The point of Series II at T = 61.08°K. is high by about 1% due probably to this lack of thermal equilibrium. The points of Series III are slightly lower than the points of Series II in the region of poor equilibrium. We believe that the slow attainment of thermal equilibrium was due to the difficult process of molecular rearrangement to give the equilibrium number of random end for end orientations.

Heat of Fusion.—Table VI gives a summary of the measurements on the heat of fusion. Each measurement started a short interval below the melting point and ended somewhat above the melting point. Correction was made for the $\int C_p dT$ and the premelting effect.

TABLE VI

HEAT OF FUSION OF CARBONYL SULFIDE

Molecular weight, 60.065

Temperature interval	Corrected heat input/mole	$\int C_p dT$ + premelting heat effect	ΔH cal./mole
132.477–138.090	1246.5	117.0	1129.5
133.730–138.186	1223.9	94.5	1129.4
132.054–137.807	1248.2	117.8	1130.4
		Mean	1129.8 ± 1.0 cal.

Heat of Vaporization.—The heat of vaporization was measured using the constant pressure regulator mentioned in the paragraph under the measurement of amount of carbonyl sulfide. Table VII contains a summary of the heat of vaporization measurements.

TABLE VII

HEAT OF VAPORIZATION OF CARBONYL SULFIDE

Boiling point, 222.87°K.; molecular weight, 60.065

Moles vaporized	Time of energy input, minutes	ΔH at 760 mm. cal./mole
0.21247	40	4424
.20469	40	4422
.20050	40	4423
.20396	40	4421
	Mean	4423 ± 4 cal.
From vapor pressure Equation 1, assuming a Berthelot gas		4415

The heat of vaporization may be calculated using the vapor pressure data and Berthelot's equation of state of the gas in connection with the equation $\Delta H = (dP/dT)(T\Delta V)$. The expression for ΔH finally takes the form

$$\Delta H = \frac{dP}{dT}\frac{RT^2}{P}\left[1 + \frac{9PT_c}{128P_cT}\left(1 - 6\frac{T_c^2}{T^2}\right) - \frac{PV}{RT}\text{liq.}\right]$$

$T_c = 378.1$°K., $P_c = 61$ atmospheres.[10]

The resulting value for ΔH is 4415 cal./mole. The heat of vaporization, assuming an ideal gas, is 141 cal./mole greater than that calculated on the basis of Berthelot's equation.

The Entropy from Calorimetric Data.—A summary of the calculation of the entropy of carbonyl sulfide at its boiling point, 222.87°K., is given in Table VIII.

The close agreement between the calculated value and the calorimetric value of the heat of vaporization lends plausibility to the use of Berthelot's equation in making a small entropy correction for the change from the actual to the ideal gas state. Berthelot's equation with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ gives the following expression for the correction:

$$\Delta S = 27RT_c^3P/32T^3P_c$$

$\Delta S = S_{\text{ideal}} - S_{\text{actual}} = 0.13$ E. U. at the boiling point.

TABLE VIII

CALCULATION OF ENTROPY OF CARBONYL SULFIDE

0–15°K., Debye function $hc\nu/k = 95$	0.55
15–134.31°K., graphical	14.96
Fusion, 1129.8/134.31	8.41
134.31–222.87°K., graphical	8.66
Vaporization 4423/222.87	19.85
Entropy of actual gas at boiling point	52.43 ± 0.10 E. U.
Correction for gas imperfection	0.13
Entropy of ideal gas at boiling point	52.56 E. U.

Entropy from Molecular Data.—The entropy of carbonyl sulfide has been calculated from band spectra data and electron diffraction measurements, using the following well-known equations

$$S_{\text{Trans.}} = 3/2R \ln M + 5/2R \ln T - R \ln P - 2.300$$

$$S_{\text{Rot.}} = R \ln IT + 177.676$$

$$S = R\sum_{\nu_1, \nu_2, \nu_3}\left[\frac{x}{1 - e^x} - \ln(e^x - 1)\right]$$

where $x = hc\nu/kT$ and ν_2 has a weight of two in the summation.

The moment of inertia of carbonyl sulfide, 137×10^{-40} g. cm.^{2}, has been obtained from the electron diffraction experiments of Brockway and Cross,[11] who give as the C=O and C=S distances 1.16 ± 0.02 Å. and 1.56 ± 0.03 Å., respectively. The uncertainty in this value leads to an uncertainty of ± 0.1 E. U. in the calculated entropy. Bartunek and Barker[12] have given the following equation summarizing the vibrational energy levels.

$$E_{\text{vib.}} = 863.4V_1 + 518.95V_2 + 2050.5V_3 - 4.2V_1^2 - 0.10V_2^2 - 2.35V_1V_2 + 9.3V_1V_3 + 3V_2V_3 + 2.65l^2\text{cm.}^{-1}$$

In making the calculation, the anharmonic terms were ignored as they do not contribute appreciably to the entropy at room temperature or lower. With this approximation, the equation gives the following vibrational frequencies: $\nu_1 = 859.2$, $\nu_2 = 521.50$, $\nu_3 = 2050.5$ (in cm.$^{-1}$).

A summary of the calculation with a comparison of the experimental and spectroscopic entropies is given in Table IX.

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[10] "Int. Crit. Tables," **3**, 231 (1928).

[11] Brockway and Cross, *J. Chem. Phys.*, **3**, 821 (1935).

[12] Bartunek and Barker, *Phys. Rev.*, **48**, 516 (1935).

TABLE IX

ENTROPY OF CARBONYL SULFIDE FROM MOLECULAR DATA

		222.87°K.	298.1°K.
Translation		36.761	38.206
Rotation		15.19	15.77
Vibration		0.711	1.389
Calculated entropy		52.66 E. U.	55.37 E. U.
Experimental entropy	Actual gas	52.43 E. U.	......
	Ideal gas	52.56 E. U.	55.27 E. U.

Cross[13] has also calculated the entropy at 298.1° K. His value is 0.03 E. U. higher than the calculated value given above. The difference is due to his use of slightly different vibrational constants.

The good agreement between the entropy value obtained from the third law of thermodynamics and that calculated from molecular data and quantum statistics proves that no random molecular orientation exists in carbonyl sulfide at low temperatures.

Summary

The heat capacity of liquid and solid carbonyl sulfide has been determined from 15°K. to the boiling point.

The melting point is 134.31°K., the boiling point, 222.87°K. (0°C. = 273.1°K.). The heat of fusion is 1129.8 cal. per mole and the heat of vaporization at the boiling point, 4423 cal. per mole.

The vapor pressure of liquid carbonyl sulfide has been measured and the data are represented very closely by the equation: liquid carbonyl sulfide 161.8 to 223.8°K.

$$\log_{10}P(\text{int. cm. Hg}) = -(1318.260/T) + 10.15309 - 0.0147784T + 0.000018838T^2$$

The density of carbonyl sulfide gas at 25°C. and 1 atm. is 2.4849 ± 0.0005 g./l.

From the experimental data the entropy of the ideal gas at the boiling point was found to be 52.56 cal./deg. per mole. This may be compared with the value 52.66 cal./deg. per mole, calculated from electron diffraction measurements and spectroscopic data.

The good agreement between the experimental and calculated values of the entropy indicates that the difference in size between the oxygen and sulfur ends of the carbonyl sulfide molecule suffices to prevent random orientation of the type found in carbon monoxide and nitrous and nitric oxides at low temperatures.

BERKELEY, CALIF.

RECEIVED OCTOBER 19, 1936

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[13] Cross, *J. Chem. Phys.*, **3**, 825 (1935).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Osmotic and Activity Coefficient Data of Some Aqueous Salt Solutions from Vapor Pressure Measurements

BY ROBERT A. ROBINSON

The isopiestic vapor pressure method has been[1] applied to the determination of the activity coefficients of some alkali halides, nitrates, acetates and *p*-toluenesulfonates and of some bivalent metal sulfates. The object of this communication is to describe: (1) the determination of the activity coefficients of some thallous salts; (2) the completion of the data for the nitrates and acetates by the inclusion of figures for the rubidium and cesium salts; (3) a redetermination on some rubidium and cesium halides and (4) the extension of measurements to polyvalent electrolytes, namely, barium chloride, lanthanum chloride, aluminum sulfate and potassium ferrocyanide.

All data in this paper refer to 25°.

I. Thallous Salts.—Thallous nitrate, perchlorate and acetate were prepared by interaction between the carbonate and the corresponding acid, the first salt being recrystallized five times and the other two salts four times. They were balanced against isopiestic solutions of potassium chloride and thence the osmotic and activity coefficients calculated in the manner described previously.[1c] The densities of aqueous solutions of the perchlorate and acetate, not hitherto recorded, have also been measured. Table I gives the data relevant to these salts, γ(D. H.) being the activity coefficient calculated on the limiting Debye–Hückel equation. Eleven determinations were made on the nitrate and twelve on the perchlorate. Twenty-nine measure-

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[1] (a) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934), (b) Robinson, *ibid.*, **57**, 1161, 1165 (1935); (c) Robinson and Jones, *ibid.*, **58**, 959 (1936).

ments on the acetate were necessary to cover the concentration range up to 6 *M*, this being one of the few thallous salts which gives concentrated solutions. The activity coefficients are plotted against $\sqrt{m}$ in Fig. 1.

TABLE I

PROPERTIES OF AQUEOUS SOLUTIONS OF THALLOUS SALTS

	$TlNO_3$			$TlClO_4$		
m	φ	γ	γ(D. H.)	φ	γ	d^{25}_4
0.025	0.940	0.834	0.832	0.945	0.844	1.0033
.05	.915	.774	.770	.926	.791	1.0094
.1	.881	.698	.692	.900	.727	1.0217
.2	.833	.603	.593	.867	.649	1.0460
.3	.800	.542	.527	.842	.597	1.0699
.4	.775	.497	.477	.822	.551	1.0935
.5	..	..	..	.806	.525	1.1167

	$TlC_2H_3O_2$					
m	0.05	0.1	0.2	0.3	0.5	0.7
φ	.932	.913	.891	.877	.857	.844
γ	.801	.745	.681	.640	.586	.550
d^{25}_4	1.0077	1.0180	1.0387	1.0590	1.0989	1.1378
m		1.0	1.5	2.0	2.5	3.0
φ		.829	.816	.809	.802	.797
γ		.511	.470	.442	.420	.403
d^{25}_4		1.1940	1.2831	1.3671	1.4457	1.5193
m	3.5	4.0	4.5	5.0	5.5	6.0
φ	0.791	0.785	0.780	0.775	0.769	0.763
γ	.388	.375	.364	.353	.344	.335

From the density determinations, together with the data for thallous nitrate in the "International Critical Tables,"[2] the apparent molal volumes, Φ have been calculated. If Φ is plotted against $\sqrt{m}$, the points lie on a straight line within the limit of experimental error and consequently Φ can be represented by the equation[3]

$$\Phi = a\sqrt{m} + b$$

using the following values of the constants

$TlNO_3$	$a = 5.9$	$b = 39.5$
$TlClO_4$	$a = 5.3$	$b = 53.55$
$TlC_2H_3O_2$	$a = 4.3$	$b = 50.9$

The partial molal volume of salt will be given by

$$\overline{V}_s = (3a\sqrt{m}/2) + b$$

and the partial molal volume of water by

$$55.51\overline{V}_w = 18.07 - (am^{1/2}/2)$$

These formulas reproduce the experimental data for the nitrate and perchlorate within approximately 0.1 cc. The equation for the acetate is valid up to 3 *M* within approximately the same limit; there is no trend in the observations from the calculated curve, so that any error is probably experimental.

Thallous nitrate is remarkable in that it has a lower activity coefficient than any other uniunivalent salt at the same concentration; the values of the activity coefficient are so low that the limiting Debye–Hückel equation reproduces the experimental data at concentrations at which it would be expected that the finite radius and the variation of the dielectric constant would invalidate the limiting law. The Gronwall–La Mer–Sandved equation[4] is no more satisfactory, because in order to reproduce the experimental data it is necessary to choose a value of $a = 1.3$ Å., which is a most improbable figure.

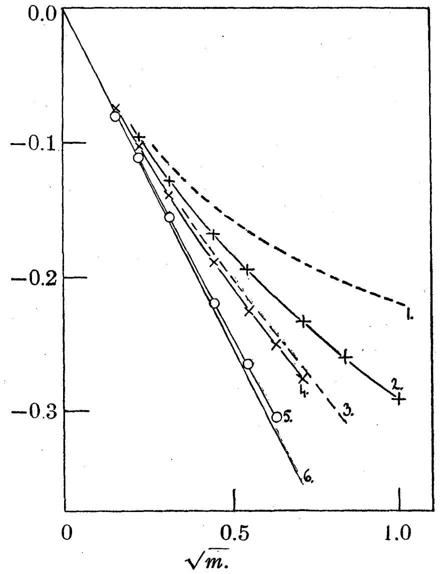

Fig. 1.—Activity coefficients of thallous salts: 1, KCl; 2, $TlC_2H_3O_2$; 3, KNO_3; 4, $TlClO_4$; 5, $TlNO_3$; 6, limiting Debye–Hückel slope.

The activity coefficient of thallous perchlorate is slightly less than that of rubidium nitrate at the same concentration and comparable with that of cesium nitrate. The data for the acetate lie between those for sodium and potassium nitrate. Thus the analogy with the heavier alkali metals exhibited by thallous nitrate and perchlorate does not extend to the acetate, for the alkali acetates are characterized by the very high values of their activity coefficients.

II. The Nitrate and Acetate of Rubidium and Cesium.—Rubidium carbonate of good quality was converted into the dichloroiodide and recrystallized twice in this form.[5] It was then converted into carbonate and the nitrate, acetate,

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[2] "International Critical Tables," Vol. III, p. 64.

[3] Masson, *Phil. Mag.*, **8**, 218 (1929).

[4] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[5] Archibald, *J. Chem. Soc.*, **85**, 776 (1904).

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF RUBIDIUM AND CESIUM NITRATE AND ACETATE

	$RbNO_3$		$CsNO_3$		$RbC_2H_3O_2$		$CsC_2H_3O_2$	
m	φ	γ	φ	γ	φ	γ	φ	γ
0.1	0.903	0.727	0.902	0.726	0.943	0.794	0.945	0.795
.2	.871	.653	.869	.648	.948	.768	.950	.770
.3	.848	.601	.843	.596	.953	.756	.956	.760
.5	.811	.532	.804	.524	.973	.757	.977	.762
.7	.782	.482	.775	.473	.992	.766	.997	.774
1.0	.745	.427	.736	.417	1.023	.792	1.026	.799
1.5	.698	.364	.685	.353	1.080	.856	1.084	.865
2.0	.656	.318	..	..	1.139	.936	1.144	.948
2.5	.620	.283	..	..	1.196	1.030	1.200	1.042
3.0	.588	.255	..	..	1.253	1.134	1.256	1.148
3.5	.562	.234	..	..	1.307	1.250	1.311	1.272
4.0	.539	.215	..	..	...	...	...	...
4.5	.517	.199	..	..	...	...	...	...

bromide and iodide prepared. Halogen analysis gave concordant values of the equivalent weight of the metal, namely, 85.38 (Rb = 85.44). Similarly cesium chloride was purified by the method described by Harned and Schupp.[6] It gave an equivalent weight of 132.75 (Cs = 132.91). From the purified material the nitrate, acetate, bromide and iodide were prepared.

The solutions of the nitrate and acetate were balanced against isopiestic solutions of potassium chloride, the number of determinations being: $RbNO_3$, 20; $RbC_2H_3O_2$, 22; $CsNO_3$ 18; $CsC_2H_3O_2$, 26. The osmotic and activity coefficients recorded in Table II were calculated. The activity coefficients of these four salts are of the magnitude which would be expected from an inspection of the data for the salts of the other alkali metals, the curves for rubidium and cesium nitrate lying close below that for potassium nitrate, while cesium acetate gives a curve above that for rubidium acetate which in turn lies above that for potassium acetate. The order of acetates, Cs > Rb > K > Na > Li is, therefore, the reverse of that which holds for alkali nitrates, chlorides, bromides and iodides.

Densities of solutions of the two acetates were also measured, but as only small quantities of material were available, small pycnometers had to be used, with a larger margin of error. The determinations should, however, be sufficient to transfer molality data to volume concentrations and to give approximate values of the coefficients in Masson's equation for the apparent molal volume. They are recorded in this manner, together with the corresponding figures for the nitrates and the remaining acetates, using data in the "International Critical Tables."[7] Similar data for the alkali halides have already been calculated by Scott.[8]

TABLE III

VALUES OF THE a AND b COEFFICIENTS

Nitrates	Li	Na	K	Rb	Cs
a	0.84	2.18	2.31	2.65	2.1
b	28.75	28.0	38.0	42.85	50.8
Acetates	Li	Na	K	Rb	Cs
a	...	2.22	2.48	2.4	2.0
b	...	39.8	47.2	53.5	61.3

III. Halides of Rubidium and Cesium.—As few measurements have been made on rubidium chloride, it was felt desirable to make another determination of the activity coefficient of this salt, using a purer specimen than was available in the previous investigation.[1a] In this work, moreover, trouble was experienced by the decomposition of the iodides of rubidium and cesium[1b] and by corrosion of the silver dishes by the more concentrated solutions. Better results have now been obtained by using chromium plated boxes of "staybrite" steel. These boxes were also used to redetermine the data for the bromides. As far as can be judged, corrosion has been eliminated, for the full amount of halogen was recoverable and there was no detectable loss in weight of the dishes even after a lengthy run. Nevertheless, a minute error assumes importance in the case of such salts whose coefficients are so close together and it is still desirable that an independent determination by another method should be made. The redetermined data are not substantially different, except in the case of rubidium iodide whose activity coefficient is slightly higher

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(6) Harned and Schupp, THIS JOURNAL, **52**, 3886 (1930).

(7) "International Critical Tables," Vol. III, pp. 78 *et seq.*

(8) Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

TABLE IV

ACTIVITY COEFFICIENTS OF RUBIDIUM AND CESIUM HALIDES

	RbCl		RbBr		RbI		CsBr		CsI	
m	φ	γ	φ	γ	φ	γ	φ	γ	φ	γ
0.1	0.923	0.761	0.922	0.760	0.921	0.759	0.917	0.751	0.916	0.750
.2	.907	.706	.905	.703	.904	.702	.896	.689	.895	.688
.3	.899	.672	.898	.671	.897	.670	.883	.650	.881	.648
.5	.891	.631	.890	.631	.888	.628	.867	.600	.865	.597
.7	.887	.605	.885	.604	.882	.600	.858	.568	.856	.564
1.0	.885	.581	.881	.577	.878	.573	.850	.535	.846	.530
1.5	.889	.557	.882	.550	.879	.546	.848	.502	.838	.493
2.0	.896	.545	.887	.535	.886	.531	.852	.484	.832	.468
2.5	.906	.538	.894	.525	.894	.523	.860	.472	.827	.448
3.0	.918	.536	.901	.519	.903	.517	.868	.464	.824	.432
3.5	.931	.537	.910	.516	.914	.516	.877	.460	..	..
4.0	.944	.539	.919	.515	.924	.515	.887	.458	..	..
4.5	.956	.542	.928	.515	.935	.517	.896	.457	..	..
5.0	.970	.545	.938	.516	.944	.518	.905	.458	..	..

TABLE V

OSMOTIC AND ACTIVITY COEFFICIENTS OF POLYVALENT ELECTROLYTES

	$BaCl_2$		$LaCl_3$		$Al_2(SO_4)_3$	$K_4Fe(CN)_6$	
m	φ	γ	φ	γ	φ	φ	γ
0.05	0.861	(0.561)	0.810	(0.380)	..	0.635	(0.189)
.1	.843	.497	.793	.325	0.420	.595	.138
.2	.835	.440	.788	.279	.390	.557	.107
.3	.836	.412	.818	.265	.391	.536	.088
.4	.842	.395	.859	.264	.422	.519	.076
.5	.8565	.388	.906	.269	.477	.507	.067
.6	.873	.384	.962	.278	.545	.498	.061
.7	.888	.383	1.010	.292	.625	.494	.055
.8	.904	.384	1.059	.317	.718	.494	.052
.9	.919	.385	1.107	.336	.810	.501	.050
1.0	.9345	.389	1.157	.358	.923	..	..
1.1	.950	.392	1.212	.385	1.037	..	..
1.2	.966	.398	1.270	.417	..	..	..
1.3	.983	.403	1.330	.454	..	..	..
1.4	1.000	.410	1.392	.495	..	..	..
1.5	1.017	.417	1.441	.535	..	..	..
1.6	1.033	.425	...	..	..	..	..
1.7	1.049	.433	...	..	..	..	..
1.8	1.064	.441	...	..	..	..	..

than that of the bromide in concentrated solutions and in the case of cesium iodide, the previous data for which differ considerably from the redetermined values. The latter are considered more reliable. This redetermination does not alter the order of the curves of γ against $\sqrt{m}$.

IV. Polyvalent Electrolytes.—Barium chloride of A. R. purity was used, analysis showing it to be of good quality. Lanthanum chloride was recrystallized three times; aluminum sulfate was prepared from A. R. potash alum and potassium ferrocyanide recrystallized once from Kahlbaum material. Table V gives the osmotic and activity coefficients derived from measurements on these four salts, numbering 36, 33, 36 and 24, respectively.

The activity coefficient of barium chloride at 0.05 M has been put equal to the value at this concentration calculated by Scatchard;[9] the present values at high concentrations are about 2% lower than those calculated by Scatchard and somewhat lower still than those derived from the measurements of Lucasse.[10] The agreement with the determinations of Pearce and Gelbach[11] is not good. For lanthanum chloride it is more difficult to select an initial value; as a temporary expedient, the activity coefficient at 0.05 M was taken as 0.380, the value for lanthanum nitrate at this concentration.[12] Similarly the value at 0.05 M for potassium ferrocyanide was taken from freezing point data.[12]

(9) Scatchard, THIS JOURNAL, **52,** 2272 (1930).

(10) Lucasse, *ibid.*, **47,** 743 (1925).

(11) Pearce and Gelbach, *J. Phys. Chem.*, **29,** 1021 (1925).

(12) Landolt-Börnstein, "Tabellen," Fifth Edition, Zweiter Ergänzungsband.

The osmotic coefficients of these salts are shown in Fig. 2 in the form of a plot of $(1 - \varphi)/z_1z_2\sqrt{\mu}$ against $\sqrt{\mu}$, z_1, z_2 being the ionic valences and μ the ionic strength. The limiting value of this function is 0.387 at 25°.

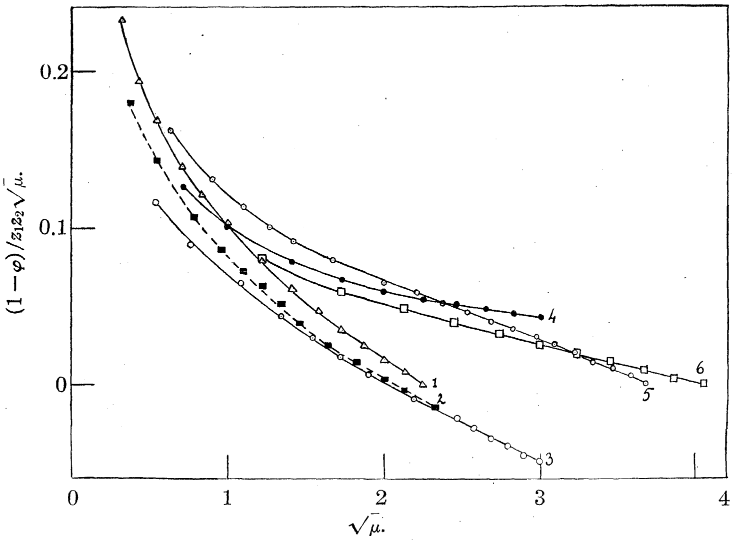

Fig. 2.—Deviation of osmotic coefficient of salt solutions from the limiting Debye–Hückel value: 1, KCl; 2, $BaCl_2$; 3, $LaCl_3$; 4, $K_4Fe(CN)_6$; 5, $ZnSO_4$; 6, $Al_2(SO_4)_3$.

Discussion

The experimental results which have been described in this and the previous papers, may be summarized qualitatively as follows. (1) The curves of γ against $\sqrt{m}$ lie in the order of I > Br > Cl for the lithium, sodium and potassium salts. This order is reversed for the rubidium and cesium salts. (2) All lithium salts have high activity coefficients, the lowest recorded being those of the *p*-toluenesulfonate. (3) With the exception of lithium nitrate, the alkali nitrates are characterized by very low activity coefficients. This is also true of sodium and potassium *p*-toluenesulfonate. (4) The alkali acetates are characterized by a reversal of the order Li > Na > K > Rb > Cs, which holds for other alkali salts. In addition, the values are all high and comparable with those of lithium salts in general. (5) Thallous salts have low activity coefficients, the nitrate having the lowest activity coefficient of any uni-univalent salt; another characteristic is to be found in the acetate which does not reproduce the behavior of the alkali acetates but has a low activity coefficient.

In another publication Professor Scatchard will discuss on the basis of his equation[13] the osmotic coefficients of the alkali halides and he will show that this equation will not only predict the magnitude of the activity coefficients within the limits anticipated but will also explain the reversal of the order I > Br > Cl for the cesium salts. Consequently I shall not enter into a discussion of these halides. It is important, however, to point out that both the constants in Scatchard's equation, which determine the variation of polarization with concentration and the non-ionic effect, respectively, are related to the molal volume of the salts.

Turning now to the thallous salts, it has been shown that the activity coefficient of the nitrate cannot be reconciled either with the limiting Debye–Hückel equation or with the Gronwall–La Mer–Sandved equation. The molal volume of thallous nitrate lies between those of rubidium chloride and bromide (39.5, 25.2 and 41.8, respectively) and its ionic radii are probably comparable with those of rubidium bromide. The disparity between the osmotic coefficients (0.800 for thallous nitrate and 0.898 for rubidium bromide at 0.3 *M*) is therefore remarkable. While an explanation in terms of a physical difference between the nitrate and halogen ions, such as the increased possibility of polarization of the latter by oppositely charged ions, cannot be excluded, it seems improbable since a like disparity between lithium nitrate and lithium bromide with osmotic coefficients of 0.941 and 0.951 at 0.3 *M*, is not found. This leaves the possibility of the incomplete dissociation of thallous nitrate to be considered. Onsager[14] has already shown that conductivity data in very dilute solutions agree with the hypothesis of incomplete dissociation in the case of potassium nitrate, thallous nitrate and thallous chloride, with dissociation constants of 1.3, 0.55 and 0.31, respectively. Similarly Redlich and Rosenfeld[15] assign a dissociation constant of 1.2 to nitric acid and Cowperthwaite, La Mer and Barksdale[16] have also used this hypothesis to account for some anomalous e. m. f. data for thallous chloride, which otherwise lead to impossibly

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[13] Scatchard, *Physik. Z.*, **33**, 22 (1932).

[14] Onsager, *ibid.*, **28**, 277 (1927).

[15] Redlich and Rosenfeld, *Monatsh.*, **67**, 223 (1936).

[16] Cowperthwaite, La Mer and Barksdale, This Journal, **56**, 544 (1934).

low values for the ionic radii. Unfortunately the data for thallous nitrate apply to concentrations too high to be dealt with by Onsager's method but Davies[17] has devised an extension of the conductivity equation to which many uni-univalent salts conform up to molar concentration, *viz.*

$$\lambda_{\text{calcd.}} \sqrt{\eta} = \lambda_0 - (0.2238\ \lambda_0 + 50.49)f(c)$$

where η is the viscosity and $f(c)$ is an empirical function of the concentration. This equation applies at 18° but it can be used at 25° if suitable alteration is made in the numerical magnitude of the constants. In spite of its empirical nature, this theory deserves consideration for it satisfies the available data for all the alkali chlorides, bromides and iodides using the same values of $f(c)$ for each salt and indeed can be extended to even higher concentrations than were originally considered by Davies. In the case of an incompletely dissociated salt Davies assumes that the degree of dissociation is given by $\alpha = \lambda_{\text{obsd.}}/\lambda_{\text{calcd.}}$ and thence the dissociation constant by

$$K = \gamma^2\alpha^2c/(1 - \alpha)$$

The conductivity data for thallous nitrate are not as extensive as could be desired but they give the following values of the dissociation constant.

m	0.01	0.02	0.05	0.1	0.2	0.25
α	.983	.972	.946	.911	.870	.848
K	.45	.48	.48	.44	.38	.36

The values of K are as constant as can be expected in view of the large variation in $(1 - \alpha)$ caused by a slight error in α. It remains now to be shown that such incomplete dissociation accords with the anomalous osmotic coefficients. The vapor pressure lowering, from which the osmotic coefficient was calculated, may be assumed to be due to two factors, one due to the ions and the other to the undissociated molecules. The relative lowering of the vapor pressure due to the latter may be taken as 0.018 m_v, m_v being the molality of the undissociated molecules, provided they can be assumed to act as a perfect solute. The osmotic coefficient of the solution in the absence of these undissociated molecules would therefore be given by

$$\varphi' = -55.51/2m_{\pm} \ln\left[(p + 0.018m_vp_0)/p_0\right]$$

where $m_{\pm}$ is the ionic molality. Calculating φ' in this manner we obtain the following values

m	0.01	0.02	0.05	0.1	0.2	0.25
φ'	.969	.959	.938	.918	.882	.871

These values are of the right order; they can not be regarded as quantitatively reliable but it is nevertheless significant that Davies' method of computing the degree of dissociation leads to osmotic coefficients which correspond to reasonable ionic dimensions.

In the case of cesium, rubidium, potassium and sodium nitrate, although their activity coefficients are not as low as in the case of thallous nitrate, yet it would be anticipated from a comparison of their molal volumes with the data for the bromides that their activity coefficients would be of the same order as those of the corresponding bromides. From this point of view the anomalies are most pronounced, especially as lithium nitrate has an activity coefficient not greatly different from that of lithium bromide. The ratios of the activity coefficient of the bromide to that of the corresponding nitrate at 1 *M* concentration are as follows

Li	Na	K	Rb	Cs
1.09	1.27	1.40	1.35	1.28

Moreover, it may be significant that conductivity data, interpreted on the basis of Davies' equation, correspond to complete dissociation of lithium nitrate; on the other hand, incomplete dissociation is indicated in the case of the nitrates of sodium, potassium and cesium (the necessary data for the rubidium salt are lacking). It is therefore tempting to ascribe the anomalous activity coefficients of these nitrates to incomplete dissociation, the most powerful argument against this hypothesis being found in the work of Rao[18] who showed that the Raman spectrum from a solution of sodium nitrate showed no lines which could be ascribed to the undissociated molecule. The argument, however, cannot be held to be conclusive until much further work has been done, for Woodward[19] has found an example in hydrofluoric acid of an electrolyte which is certainly incompletely dissociated but gives no Raman lines for the undissociated molecule. Applying Davies' equation to these three nitrates, the following results are obtained.

Molality	0.01	0.05	0.1	0.5	1
			$NaNO_3$		
α	0.996	0.985	0.982	0.947	0.913
K	2.0	2.0	3.0	3.2	2.9
φ'	0.978	0.943	0.912	0.898	0.880

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[17] Davies, *Trans. Faraday Soc.*, **23**, 354 (1927).

[18] Rao, *Proc. Roy. Soc.* (London), **144**, 159 (1934).

[19] Woodward, *Physik. Z.*, **32**, 777 (1931).

Molality	0.01	0.05	0.1	0.5	1
KNO_3					
α	0.991	0.973	0.959	0.895	0.845
K	.87	1.09	1.19	1.11	.91
φ'	.978	0.947	0.919	0.855	.803
$CsNO_3$					
α	0.991	0.966	0.948	0.877	0.821
K	.87	.85	.91	.86	.66
φ'	.978	.950	.924	.839	.784

Whilst these osmotic coefficients can have little quantitative significance, especially for more concentrated solutions, the purpose of the calculation is achieved by showing that the effect of incomplete dissociation is such as to lead to osmotic coefficients of a more reasonable order.

The osmotic coefficients of the alkali acetates are much higher than one would expect from a consideration of their molal volumes. Davies' equation, however, gives no indication of incomplete dissociation and it is probable that the abnormally high values for all but the lithium salt as well as the reversal in the normal order Li > Na > K > Rb > Cs will find an explanation in the asymmetrical distribution of charge in the acetate ion.

There seems to be no purpose at present in attempting a theoretical explanation of the coefficients of the polyvalent salts. It may, however, be pointed out that, as Fig. 2 shows, the departure from the limiting Debye–Hückel equation at high concentrations is no more marked for polyvalent electrolytes in general than it is for a typical uni-univalent salt such as potassium chloride.

Finally I wish to record my thanks to Professor G. Scatchard, who has helped me with much information regarding his theory and to the Chemical Society for a grant which assisted in the purchase of rubidium and cesium salts.

Summary

1. Osmotic and activity coefficients have been determined by the isopiestic vapor pressure method for thallous nitrate, perchlorate and acetate, rubidium and cesium nitrate and acetate, barium chloride, lanthanum chloride, potassium ferrocyanide and aluminum sulfate. The data for rubidium chloride, bromide and iodide and cesium bromide and iodide have been redetermined.

2. The possibility of incomplete dissociation of sodium, potassium, cesium and thallous nitrate has been discussed and it is shown that not only is this hypothesis consistent with Davies' extension of the conductivity equation but it also explains the abnormally low values found for the osmotic and activity coefficients of these salts.

AUCKLAND, NEW ZEALAND RECEIVED AUGUST 12, 1936

[A CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE OHIO STATE UNIVERSITY]

The Use of Crotonaldehyde to Reduce the Postprecipitation of Zinc on Copper Sulfide

BY JOHN R. CALDWELL[1] AND HARVEY V. MOYER

It has been known for many years that copper sulfide, precipitated in the presence of zinc, will carry down appreciable quantities of zinc even when the precipitation is made in a normal acid solution. Various theories of mixed crystal formation, of solid solution and of coprecipitation have been proposed as explanations. Comparatively recent studies have been made by Kolthoff and Pearson,[2] Knowles and Martin,[3] Balarew[4] and Kolthoff and Moltzau.[5]

Kolthoff has presented evidence which seems to indicate that an adsorbed layer of hydrogen sulfide on the surface of the copper sulfide causes the postprecipitation of the zinc as sulfide.

Recently we have found that certain organic compounds may be used to alter the nature of analytical precipitates.[6–9] In a study of the separation of zinc and cobalt, it was found that if zinc sulfide was precipitated in the presence of a small amount of certain aldehydes, acrolein in particular, the quantity of cobalt carried down is

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(1) Present address, Tennessee Eastman Corporation, Kingsport, Tennessee.

(2) Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

(3) Knowles and Martin, *Trans. Faraday Soc.*, **31**, 502 (1935).

(4) Balarew, *Z. anal. Chem.*, **102**, 408 (1935).

(5) Kolthoff and Moltzau, *Chem. Rev.*, **17**, 293 (1935).

(6) Caldwell, THIS JOURNAL, **57**, 96 (1935).

(7) Caldwell and Moyer, *ibid.*, **57**, 2372 (1935).

(8) Caldwell and Moyer, *ibid.*, **57**, 2375 (1935).

(9) Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

so small that it is possible to make a quantitative separation of the metals in one precipitation. It seemed quite probable that this same procedure could be applied to the separation of copper and zinc.

Although a number of aldehydes were found to be effective in reducing the postprecipitation of zinc on copper sulfide, the unsaturated aldehydes containing the structure, RCH=CHCHO, proved superior to all others tried. Acrolein, cinnamic aldehyde and crotonaldehyde contain this structure and all were found to reduce greatly the quantity of zinc carried down. Acrolein is probably the best but it is troublesome to prepare and polymerizes so readily that it is difficult to keep. Cinnamic aldehyde tends to form an insoluble resinous product which interferes with filtration. Crotonaldehyde does not have these objectionable properties and was chosen for this investigation although it is not as effective as acrolein in the separation of zinc from cobalt. Benzaldehyde and formaldehyde were tried but were not as satisfactory as the unsaturated aldehydes. It was found that formaldehyde was quite effective in reducing the quantity of zinc carried down, but it seemed to prevent the quantitative precipitation of the copper. A few tenths of a milligram of copper always remained in solution after saturation with hydrogen sulfide.

Experimental

Materials.—The benzaldehyde and crotonaldehyde were distilled through a small laboratory fractionating column. Formaldehyde was used in the usual 40% solution.

A reagent grade of copper sulfate was recrystallized twice.

A reagent grade of zinc sulfate was recrystallized once.

Procedure.—A solution containing 0.125 g. of zinc and 0.125 g. of copper as sulfates with varying quantities of sulfuric acid was diluted to 100 ml. in a 250-ml. Erlenmeyer flask. Precipitations were made in pairs, one without aldehyde and the other containing approximately 0.05 ml. of an aldehyde. The flasks were connected to the same source of hydrogen sulfide through a Y-tube to ensure an equal supply of gas to each solution. A mechanical shaker kept the solutions in constant agitation during precipitation. Hydrogen sulfide was passed into the open flasks for five minutes to remove the air, then the flasks were stoppered and the gas was kept in contact with the solutions for fifteen minutes at the pressure of about 15 cm. of water. The flasks were removed, stoppered and allowed to stand for different lengths of time varying from thirty minutes to six hours.

In order to determine the quantity of zinc carried down, the solution was filtered through filter paper, washed with hot water and then five 10-ml. portions of 6 N hydrochloric acid were poured through the filter. This procedure was carried out in a hood since the aldehyde and hydrogen sulfide react to form a compound with a very unpleasant odor. The zinc was extracted by the hydrochloric acid and it was observed that if more than 10 mg. of zinc was present, there was a vigorous evolution of hydrogen sulfide. A few milligrams of copper always dissolved and this was removed before the zinc was determined. The solution was evaporated to dryness, moistened with nitric acid and again brought to dryness to destroy organic matter. The residue was dissolved in 100 ml. of water which was made normal with hydrochloric acid and the trace of copper precipitated with hydrogen sulfide. After filtration, the solution was evaporated to dryness and the zinc was determined turbidimetrically with potassium ferrocyanide according to the method described by Yoe.[10] In order to be certain that all the zinc was extracted from the copper sulfide, several precipitates, some formed in the presence of aldehyde and some formed in its absence, were dissolved in nitric acid and reprecipitated in the presence of crotonaldehyde. No zinc was found in any of the filtrates.

Benzaldehyde was tried in the first quantitative experiments. Although copper sulfide is usually precipitated in a solution 0.5 to 1 N in sulfuric acid, a lower normality was chosen in order to bring out the protective action of the aldehydes to the fullest extent. In the presence of 0.05 ml. of benzaldehyde, the zinc carried down with the copper sulfide varied from 0.2 to 1.2 mg., whereas, in the absence of the aldehyde, the quantity of zinc varied from 1.5 to 15 mg. Although considerable reduction in the zinc carried down was brought about by the benzaldehyde, it was not considered a satisfactory protective agent because of rather large variations in the results.

Crotonaldehyde was found to be effective in reducing the post-precipitation of zinc even in 0.36 N acid. In a series of determinations carried out as described above, approximately seventy times as much zinc was found on an average in the copper sulfide precipitates which were formed in the absence of the aldehyde. In four determinations in which filtration was made immediately after precipitation, an average of 0.07 mg. of zinc was found in those precipitated with aldehyde and an average of 4.0 mg. was found in the blanks. In ten determinations in which the precipitates were allowed to stand from two to three hours, an average of 0.11 mg. of zinc was found in those treated with aldehyde and an average of 8.0 mg. was found in the untreated ones. Five determinations on standing from four to six hours showed an average of 0.25 mg. of zinc when precipitated with aldehyde and an average of 18.0 mg. in its absence. A change of acid concentration from 0.36 to 0.5 N caused no significant difference in the results.

Discussion

The study of the postprecipitation of zinc on copper sulfide is complicated by the fact that the precipitate of copper sulfide is variable in composition and its true chemical nature is still unknown. Feigl[11] believes the initial precipitate

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[10] Yoe, "Photometric Chemical Analysis," John Wiley and Sons, Inc., New York, 1928, p. 397.

[11] Feigl, *Z. anal. Chem.*, **72**, 32 (1927).

contains free sulfur because boiling with sodium sulfite gives a considerable quantity of sodium thiosulfate. Recent work by Sauer and Steiner[12] lends support to this view. There is a definite cycle of changes which take place during the precipitation and aging of copper sulfide. During early stages of the precipitation, copper sulfide separates as a fine black sol which remains in suspension in the solution. After three or four minutes the particles begin to clump together and settle. In another five minutes the loose clumps become more compact and dense and assume a brownish color. If the flask is stoppered and allowed to stand, a definite aging process takes place. In two or three hours, the dense brownish-black aggregations begin to disperse and become greenish-black in color. In about ten hours the peptization has reached a point where secondary aggregates are so reduced in size as to be almost invisible to the unaided eye. Microscopic examination shows that minute primary particles predominate. An extremely small concentration of crotonaldehyde exerts a profound influence upon this aging process. When formed in the presence of crotonaldehyde, the precipitate does not peptize to give small primary particles, but on the contrary tends to coagulate into clumps that are even larger than those formed in the beginning. Microscopic examination shows that the clumps consist of many primary particles closely packed into opaque dense masses which show no tendency to disintegrate, even after standing for several days.

Summary

If copper sulfide is precipitated in the presence of a very small concentration of crotonaldehyde, the quantity of zinc carried down is reduced greatly. Apparently the crotonaldehyde reacts with the adsorbed hydrogen sulfide and reduces its value on the surface of the copper sulfide so that it will not cause the postprecipitation of the zinc.

COLUMBUS, OHIO RECEIVED SEPTEMBER 4, 1936

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(12) Sauer and Steiner, *Kolloid-Z.*, **72**, 41 (1935).

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Conductivity of Various Salts in *n*-Propyl and Isopropyl Alcohols

BY FRANK HOVORKA AND JOHN COLBERT SIMMS[1]

Introduction

The conductivity of various salts has been determined in methyl and ethyl alcohols by many workers during the last few years. Since only a comparatively few measurements were made in *n*-propyl and isopropyl alcohols, it seemed desirable to carry out a series of conductivity determinations of the more common uni-univalent salts in these two solvents. The dielectric constant of the alcohols gradually decreases as they increase in molecular weight. Therefore, a study of the alcohols as a series ought to give the effect of the solvent as well as that of the dielectric constant on the nature of the electrolytic solutions.

Apparatus.—The assembly comprised a Leeds and Northrup Kohlrausch bridge and dial box type coils of low induction. All the resistances were checked against coils calibrated by the Bureau of Standards. The balance point was detected by Baldwin type telephones using two stage amplification. The other parts used in this "set up" were of the standard type generally used in accurate conductivity measurements.

The cell used in this investigation was of borosilicate glass and was made after a design of Hartley and Barrett.[2]

The thermostat was a large vacuum jar. The temperature was kept constant at 25 ± 0.005°.

Materials and Procedure.—Each of the alcohols containing a little water was refluxed for several hours over barium oxide and then distilled into a Pyrex fractionating flask and column without coming in contact with air. Each was fractionated to a boiling point of 0.05° and then treated with metallic sodium. After two further distillations they were fractionated directly into the conductivity cell which was dried previously by passing dry warm air through it. Usually about 100 g. of alcohol was distilled into the cell. The specific resistance of the *n*-propyl alcohol was 2×10^8 mhos. and of the isopropyl alcohol 9×10^9 mhos. These values were determined by using a direct current of 135 volts and were used in making the solvent correction.

The C. P. salts were recrystallized from water at least three times, dried, and analyzed for final purity. A known amount of each salt was transferred to a 100-cc. Pyrex bottle which had been baked out with a free flame. All of the handling of salts as well as of the alcohols was car-

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(1) This communication is an abstract of a portion of a thesis submitted by John Colbert Simms in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry. Original manuscript received July 24, 1933.

(2) Hartley and Barrett, *Trans. Chem. Soc.*, **103**, 789 (1913).

ried out in an atmosphere of dry air. Enough alcohol from the final purification was distilled into this bottle to give about a thirtieth normal solution. A small weight pipet was filled from this bottle and introduced through the cap of the cell while dry air was passing through the cell. The addition of about one gram of this solution to about 100 g. of the alcohol gave a solution approximately 0.0001 *N*.

The electrodes finally used were coated with a medium layer of platinum black and ignited to redness. This gave a dull gray coating. The balance was quite easily obtained and no oxidation seemed to occur as the conductivity of the solutions did not change on standing.

The value of the cell constant was determined several times during the work and no variation greater than the experimental error could be noted. The measurements were made over the same range of concentration as that of the alcohol solutions. Water was weighed in the cell and an aqueous solution of potassium chloride was added through the weight pipet. The conductivity values found compared with those calculated by the Kohlrausch and Maltby equation as corrected by Kraus and Parker:[3] $\Lambda_c = 129.91 - 80.75\sqrt{c}$.

Before the measurements on propyl alcohol were begun Frazer and Hartley's[4] measurements on potassium chloride were repeated. The results obtained checked their conductivity curve well within the experimental error.

Results

In Tables I and II C is the equivalent concentration; Λ_c the experimental equivalent conductivity; K_1, the dissociation constant as calculated from the Ostwald dilution law; and K_2, the dissociation constant as computed by the Fuoss and Kraus[5] method where

$$K_2 = c\gamma^2 f^2/1 - \gamma$$

c is the equivalent concentration, γ is equal to the average fraction of solute free to carry the current and f is the activity coefficient of the ions expressed by

$$-\ln f = \beta\sqrt{c\gamma}/(1 - \delta\sqrt{c\gamma})$$

$$\text{where } \beta = \frac{e}{2DkT}\left(\frac{8\,Ne^2}{1000\,DkT}\right)^{1/2}$$

$$\text{and } \delta = \left(\frac{8\,Ne^2}{1000\,DkT}\right)^{1/2}\alpha$$

TABLE I

CONDUCTIVITY AND DISSOCIATION CONSTANTS IN *n*-PROPYL ALCOHOL

$C \times 10^4$	Λ_c	$K_1 \times 10^3$	$K_2 \times 10^3$
Potassium iodide			
Series A			
2.842	22.39	1.998	3.950
5.202	21.19		
8.429	20.12		
12.260	19.07	2.980	4.229
Series B			
2.588	22.61		
3.273	22.08		
5.068	21.33	2.393	4.082
17.980	18.09		
Series C			
1.037	23.70		
1.581	23.23	1.778	4.166
4.122	21.75		
9.136	19.91	2.742	4.110
14.530	18.55		
16.140	18.29		
Sodium iodide			
Series A			
2.255	21.98	2.322	7.022
5.050	20.80		
9.133	19.66	3.445	6.985
15.770	18.42		
Series B			
4.299	21.05	2.753	6.513
9.125	19.72		
17.240	18.12		
Series C			
2.989	21.50		
7.399	19.95		
11.161	19.23	3.661	7.515
25.931	17.36		
Sodium bromide			
Series A			
1.645	16.91		
2.930	16.38	2.224	9.386
5.126	15.73		
8.410	15.08	3.235	9.548
Series B			
2.772	16.58		
5.958	15.61	2.936	9.430
10.560	14.69	3.438	9.913
17.281	13.68	3.816	9.636
Potassium bromide			
1.303	20.98	1.283	2.434
1.732	20.53	1.326	2.263
4.760	18.57	1.642	2.284
7.190	17.60	1.822	2.389

Each term has the usual significance. In calculating β and δ and later α the dielectric constants determined by Åkerlöf[6] were used. α, the mean value of the ionic radius, was obtained from the Stokes law.[7] The viscosities for the two solvents were obtained by evaluating the data of

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[3] Kraus and Parker, THIS JOURNAL, **44**, 2422 (1922).

[4] Frazer and Hartley, *Proc. Roy. Soc.* (London), **A109**, 351 (1925).

[5] Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

[6] Åkerlöf, *ibid.*, **54**, 4125 (1932).

[7] Newman, "Electrolytic Conduction," J. Wiley and Sons. Inc., New York, 1931, p. 126.

TABLE II

CONDUCTIVITY AND DISSOCIATION CONSTANTS IN ISOPROPYL ALCOHOL

$C \times 10^4$	Λ_c	$K_1 \times 10^3$	$K_2 \times 10^3$
Potassium iodide			
Series A			
2.478	19.61		
3.407	18.77		
7.522	16.55	1.274	1.441
9.732	15.71	1.323	1.539
Series B			
1.420	20.57		
2.848	19.20	1.054	1.394
5.566	17.52	1.229	1.469
11.931	15.16		
Sodium iodide			
Series A			
1.988	16.61	1.498	4.124
3.856	15.59		
6.137	14.78		
10.191	13.75	2.147	3.762
Series B			
2.680	16.21	1.599	3.897
7.371	14.44	1.998	3.701
20.040	11.82		
Sodium bromide			
Series A			
3.276	15.24	1.196	1.839
6.200	13.96		
8.291	13.21	1.426	1.871
12.880	12.04	1.515	1.856
25.830	9.99		
Series B			
5.351	14.16	1.281	1.772
17.711	11.12		
18.561	10.87		
Potassium bromide			
Series A			
2.308	13.65	3.524	3.679
3.634	12.26	3.650	3.653
5.134	11.18		
Series B			
3.160	12.57	3.482	3.511
4.161	11.66	3.424	3.442

Gartenmeister,[8] Thorpe and Rodger,[9] and Dunston and Thole.[10]

Series A, B, etc., indicate results of entirely independent runs.

Table III gives the values of the constants used for various salts in the two solvents.

TABLE III

CONSTANTS FOR CONDUCTANCE CURVES AT 25°

Solute	α	β	$a \times 10^8$	δ
n-Propyl alcohol				
Diel. constant = 20.1 Viscosity = 0.0199				
Potassium iodide	98.52	3.907	3.222	2.093
Sodium iodide	96.21	3.907	3.397	2.206
Sodium bromide	86.37	3.907	4.408	2.864
Potassium bromide	95.18	3.907	3.480	2.260
Isopropyl alcohol				
Diel. constant = 18.0. Viscosity = 0.02072				
Potassium iodide	109.86	4.612	3.328	2.286
Sodium iodide	100.11	4.612	4.149	2.851
Sodium bromide	98.28	4.612	4.351	2.989
Potassium bromide	101.23	4.612	4.034	2.772

In Table IV Λ_0 is the limiting conductivity obtained by extrapolating $\Lambda_c - \sqrt{c}$ experimental curves. Λ_0' was obtained by using the Fuoss and Kraus[5] equation

$$\gamma' = \frac{\Lambda/\Lambda_0}{1 - \alpha\Lambda_0^{-3/2}\sqrt{C\Lambda}}$$

and determining for what value of Λ_0, γ will converge to a constant value as successive substitutions are made. α in the last expression is computed by Onsager[11] as $\alpha = \frac{8.18 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{82}{\eta(DT)^{1/2}}$

This is probably the best method for obtaining accurately the limiting equivalent conductivity. A greatly simplified method for estimating γ suggested later by Fuoss[12] was found to be very useful but was not as accurate for the determination of Λ_0 as the original method which was used in all of the calculations in this paper. K_1 and K_2 are the averages of those given in Tables I and II. K_3 is a dissociation constant obtained by plotting $f\sqrt{c} - \sqrt{1 - \gamma}/\gamma$ for various values of Λ_0 until a straight line is obtained which passes through the origin. The slope of this line is equal to K_3.

Discussion

When $\Lambda_c - \sqrt{c}$ curves are plotted the points fall quite well on a straight line up to a concentration of about 0.0003 *N*. Above this concentration region the equivalent conductivity decreases at a considerably lower rate with the increase in concentration. Many of the curves intersect, illustrating rather marked differences between the electrolytes. These differences become more evident with the increasing molecular weight of the alcohols. In methyl alcohol, for instance,

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[8] Gartenmeister, *Z. physik. Chem.*, **6**, 524 (1890).

[9] Thorpe and Rodger, *Trans. Roy. Soc.* (London), **A185**, 397 (1895).

[10] Dunston and Thole, *J. Chem. Soc.*, **95**, 1556 (1909).

[11] Onsager, *Physik. Z.*, **28**, 277 (1927).

[12] Fuoss, THIS JOURNAL, **57**, 488 (1935).

which resembles water in its behavior, the curves are almost parallel.

The experimental slopes of the conductivity curves are greater in every case than those predicted by Onsager. The deviation is in the neighborhood of 100% or more indicating a rather incomplete dissociation. The comparison of the values of experimental Λ_c (Tables I and II) with those calculated from the Debye–Hückel–Onsager equation show differences of about 5 to 10% in the more dilute regions.

The limiting equivalent conductivity (Table IV) of each salt is considerably less than its conductivity in ethyl alcohol. However, if methyl, ethyl, and the propyl alcohols are considered as a series, the values obtained cannot be explained on the ground of viscosity and the dielectric constant differences. Further, there seems to exist no relation in the order of conductivities of the salts in propyl and isopropyl alcohols, nor does the principle of additivity apply in either alcohol. Either the chemical nature of the solvent plays an important part or the viscosity and the dielectric constant are not accounted for correctly or both. It is of interest to note that the values of Λ_0 obtained by the extrapolation of $\Lambda_c - \sqrt{c}$ curves and those obtained by the Fuoss and Kraus method differ in some cases by as much as 3%. The importance, of course, of obtaining correct Λ_0 for various calculations cannot be overemphasized.

TABLE IV

LIMITING CONDUCTIVITY AND DISSOCIATION CONSTANTS

Solute	Alcohol solvent	Λ_0	Λ_0'	$K_1 \times 10^3$	$K_2 \times 10^3$	$K_3 \times 10^3$
KI	*n*-Propyl	25.42	25.16	2.378	4.107	4.053
NaI	*n*-Propyl	24.12	23.94	3.046	7.010	7.039
NaBr	*n*-Propyl	18.58	18.31	3.054	9.582	9.140
KBr	*n*-Propyl	23.54	22.93	1.518	2.343	2.373
KI	Isopropyl	23.64	23.45	1.220	1.461	1.461
NaI	Isopropyl	18.96	18.58	1.811	3.846	3.798
NaBr	Isopropyl	18.08	18.65	1.354	1.835	1.853
KBr	Isopropyl	19.50	19.81	0.352	0.357	0.354

There seem to be data available only for sodium iodide in propyl[13] and isopropyl alcohols.[14] The value of 18.87 obtained for Λ_0 by Brown for sodium iodide in isopropyl alcohol is in good agreement with the value obtained here. However, the value of 21.04 for Λ_0 obtained by Keyes and Winninghoff for sodium iodide in propyl alcohol is in considerable disagreement with the value found here.

The dissociation constants (Table IV) show that all of the salts used here may be considered as weak electrolytes in propyl and isopropyl alcohol. The values of these constants fit in rather well with those recorded for the lower and higher alcohols as well as for related solvents.[15]

The variation of the dissociation constant with concentration is shown in Tables I and II. The method of Fuoss and Kraus yields much greater but quite constant values. The Ostwald dilution law gives values for dissociation constants that increase considerably with the increase in concentration. The former is expected while the latter is inconsistent for weak electrolytes.

Summary

The conductivities of potassium iodide and bromide and of sodium iodide and bromide have been determined in propyl and isopropyl alcohols.

The limiting equivalent conductivities were calculated by the Fuoss and Kraus method and were compared with those obtained by extrapolation of $\Lambda_0 - \sqrt{C}$ curves.

The dissociation constants were calculated by the Fuoss and Kraus, and Ostwald methods for each electrolyte. It was shown that the former method yields greater but quite constant values. Furthermore, the values of the dissociation constants indicate that all of the salts used here may be considered as weak electrolytes in propyl and isopropyl alcohols.

There seems to exist no relation in the order of conductivities of the salts in these two alcohols nor does the principle of additivity apply in either alcohol.

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(13) Keyes and Winninghoff, THIS JOURNAL, **38**, 1178 (1916).

(14) Brown, Thesis, Yale University, 1929.

(15) See Davies, "The Conductivity of Solutions," J. Wiley and Sons, Inc., New York, 1930, pp. 197–199, for a complete bibliography of accurate conductivity measurements in non-aqueous solutions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Effect of Structure upon the Reactions of Organic Compounds. Benzene Derivatives

BY LOUIS P. HAMMETT

The effect of a substituent in the meta or para position of the benzene ring upon the rate or upon the equilibrium of a reaction in which the reacting group is in a side chain attached to the ring may be represented by a simple formula which is valid within a reasonable precision in a surprising variety of cases. The formula is

$$-RT \ln K + RT \ln K^0 = \Delta F = A/d^2 \left(\frac{B_1}{D} + B_2\right)$$

K is a rate constant or an equilibrium constant for a substituted reactant, K^0 is the corresponding quantity for the unsubstituted reactant, ΔF is a free energy change or its kinetic analog, d is the distance from the substituent to the reacting group, D is the dielectric constant of the medium in which the reaction occurs, and the quantities A, B_1 and B_2 are constants independent of temperature and solvent. Of these A depends only upon the substituent and its position in the ring relative to the reacting group (with one exception, the two values necessary for the para nitro group), while B_1 and B_2 depend only upon the reaction.

The most important practical feature of equation (1) is the separation of the effect of a substituent into two constants, one of which depends on the substituent, the other upon the reaction. For this corollary of the equation the linear logarithmic relationships between equilibrium and rate constants which have been noted by myself[1] and in wider variety by Burkhardt, Ford and Singleton[2] offer a verification which has so far been made only qualitatively and by graphical methods. A more significant test may be made by obtaining a set of values of the constant A for various substituents from some suitable reaction or reactions, and determining quantitatively the precision with which these constants may be made to fit the data for all available reactions. For this purpose equation (1) may be rearranged to the form

$$\log K = \log K^0 + \sigma\rho \qquad (2)$$

$$\text{where } \sigma = -A/2.303\ R$$

$$\rho = \frac{1}{d^2 T}\left(\frac{B_1}{D} + B_2\right)$$

σ is a substituent constant, dependent upon the substituent; ρ is a reaction constant, dependent upon the reaction, the medium and the temperature. Since the only data available consist of values of the $\sigma\rho$ product, it is necessary to assign an arbitrary value to some one σ or ρ. The choice of a value of unity for the ρ constant in the ionization equilibrium of substituted benzoic acids in water solution at 25° was determined by the large amount of accurate data availabe from the recent work of Dippy and co-workers.[3] On this basis the difference between the logarithm of the ionization constant of a substituted benzoic acid and the logarithm of the ionization constant of benzoic acid gives the value of the σ constant for that substituent. With the nucleus of σ values thus provided, ρ values have been derived by least squares methods for other reactions, and from these in turn σ values have been obtained for substituents whose effects upon the ionization constant of benzoic acid are unknown or inaccurately known. After any new σ value was obtained it was used for the calculation of subsequent ρ values, so that the order of the calculations, which is that of the key numbers in the Tables, is of some significance. The criterion of the validity of equations (1) or (2) for any reaction is the precision with which the previously determined values of σ together with the experimental values of log K satisfy the linear equation (2). As a measure of this precision I have used the median deviation of the experimental points from the best straight line, the "probable error" of a point.[4]

The results of such calculations for all the reactions I have been able to find are given in Tables I, II and III. Table I contains the values of the substituent constants σ together with the symbol of the substituent, a key number to indicate the reaction from which the value was obtained, the number of reactions n for which data on the effect of this substituent are available, and the probable

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(1) Hammett, *Chem. Rev.*, **17**, 125 (1935).

(2) Burkhardt, Ford and Singleton, *J. Chem. Soc.*, 17 (1936).

(3) (a) Dippy and Williams, *ibid.*, 1888 (1934); (b) Dippy, Williams and Lewis, *ibid.*, 343 (1935); (c) Dippy and Lewis, *ibid.*, 644 (1936).

(4) Wright and Hayford, "The Adjustment of Observations." D. Van Nostrand Company, New York, 1906, p. 132.

error r of the log K values calculated for this substituent for these reactions. The data on reactions 28, 35, 36, 37 and 38 were not included in calculating the probable error because there was reason in these cases to doubt the accuracy of the measurement or the theoretical applicability of equation (1). Table II contains the ρ values for the various reactions together with a key number for the reaction, the best value of log K^0 in equation (2), the number of substituents n for which data are available, and the probable error r of the calculated values of log K. Table III contains brief descriptions of the reactions and literature references under the key numbers previously used. In the descriptions E means that the data used are the equilibrium constants of the reaction described, R that they are rate constants.

TABLE I

SUBSTITUENT CONSTANTS

Subst.	Constant σ	Source	No. of reactions n	Probable error r
$p\mathrm{NH_2}$	-0.660	2	2	...
$p\mathrm{CH_3O}$	$-$ .268	1	21	0.077
$p\mathrm{C_2H_5O}$	$-$ .25	3	6	.105
3,4-di $\mathrm{CH_3}$	$-$ .229	4	1	...
$m\mathrm{(CH_3)_2N}$	$-$ .211	31	1	...
$p\mathrm{(CH_3)_2N}$	$-$ .205	21[a]	1	...
$p\mathrm{CH_3}$	$-$ .170	1	33	.046
$m\mathrm{NH_2}$	$-$ .161	2	3	.060
$3{,}4\mathrm{CH_2O_2}$	$-$ .159	2	3	.023
$p\mathrm{C_2H_5}$	$-$ .144	2	1	...
$m\mathrm{CH_3}$	$-$ .069	1	21	.038
$p\mathrm{CH_3S}$	$-$ .047	2	1	...
None	.000	1	36	.034
$p\mathrm{C_6H_5}$	+ .009	2	3	.22
$p\mathrm{F}$	+ .062	1	7	.066
$m\mathrm{CH_3O}$	+ .115	1	7	.116
$m\mathrm{C_2H_5O}$	+ .15	3	2	...
$\beta\mathrm{C_4H_4}$[b]	+ .17	3	9	.102
$p\mathrm{Cl}$	+ .227	1	31	.040
$p\mathrm{Br}$	+ .232	1	24	.040
$p\mathrm{I}$	+ .276	2	11	.073
$m\mathrm{F}$	+ .337	1	5	.083
$m\mathrm{I}$	+ .352	1	8	.039
$m\mathrm{Cl}$	+ .373	1	19	.041
$m\mathrm{Br}$	+ .391	1	17	.035
$p\mathrm{C_6H_5N_2}$	+ .640	26, 27	1	...
$m\mathrm{CN}$	+ .678	26, 27	1	...
$m\mathrm{NO_2}$	+ .710	1	21	.069
$p\mathrm{NO_2}$(b)[c]	+ .778	1	15	.066
$p\mathrm{CN}$	+1.000	4	4	.042
$p\mathrm{NO_2}$(a)[d]	+1.27	3	8	.052

[a] A statistical factor of 2 was used in calculating the value of σ. [b] β-Naphthalene derivatives. [c] To be used for the reactions of all benzene derivatives except those of aniline and phenol. [d] To be used for the reactions of derivatives of aniline and phenol.

TABLE II

REACTION CONSTANTS

Reaction	log K^0	Constant ρ	Probable error r	No. of substituents n
1	-4.203	+1	...	14
2	-1.294	+2.498	0.067	12
3	-4.569	+2.730	.060	14
4	-9.941	+2.008	.047	5
5	-0.963	+1.267	.026	11
6	-1.410	-0.085	.118	7
7	-0.597	$-$ .550	.045	14
8	-1.746	+ .417	.060	10
9	-3.180	+1.394	.054	6
10	-1.009	+1.055	.035	13
11	-1.735	+0.118	.040	12
12	-9.699	+2.143	.065	14
13	-2.293	+1.529	.104	13
14	-1.585	+1.471	.065	10
15	-1.201	+1.217	.035	4
16	+0.137	-3.690	.085	6
17	-2.121	-3.190	.073	10
18	-0.604	-2.581	.160	10
19	-1.558	-2.743	.041	6
20	-1.508	-1.088	.040	5
21	-0.944	-2.382	.057	6
22	-1.772	-2.903	.038	4
23	-1.152	-2.694	.154	5
24	+0.665	-1.453	.036	11
25	-2.345	-1.219	.034	9
26	-2.946	+0.316	.055	9
27	-3.484	+1.190	.030	4
28	-1.491	+0.796	.220	9
29	-2.536	-1.799	.080	6
30	-0.698	-0.946	.043	9
31	-1.142	$-$ .771	.046	9
32	-2.177	$-$ .991	.016	5
33	-4.076	+ .587	.037	10
34	-1.921	+2.142	.054	7
35	-0.035	+0.824	.071	6
36	-4.288	+0.471	.026	10
37	-0.973	-1.875	.154	12
38	+0.167	+0.785	.078	11
39	-0.018	+2.240	.079	9

The verification of equation (3) is satisfactory. Out of thirty-eight reactions involving derivatives of benzoic acid, of phenol, of aniline, of benzenesulfonic acid, of phenylboric acid, and of phenylphosphine, and including both equilibrium and rate constants, there are only six for which the probable error is greater than 0.1, one only for which it is greater than 0.2, and the mean value of the probable error for the whole series of reactions is 0.067. These figures compare well with a total range in the value of log K between p-nitro and p-amino substituted derivatives which may in an extreme case (reaction 16) amount to as much as 7. Figure 1 visualizes the magnitude of the deviations because the four reactions for which log K values are plotted against the σ values from Table I show probable errors not far from the mean value.

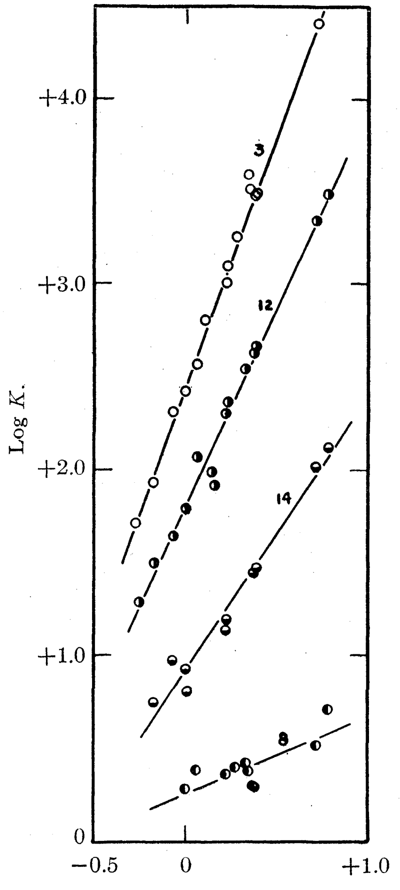

Fig. 1.—Relationship between log K and σ for various reactions (see Table III). The position of the scale of ordinates is arbitrary.

TABLE III

1. E. Ionization of substituted benzoic acids in water at 25°.[3]
2. R. Alkaline hydrolysis of substituted benzoic esters in 87.83% ethyl alcohol at 30°.[5]
3. E. Acidity constants of substituted anilinium ions in water at 25°.[6]
4. E. Ionization of substituted phenols in water at 25°.[7]
5. R. Hydrolysis of substituted cinnamic esters, conditions as in reaction 2.[5b]
6. R. Acid catalyzed esterification of substituted benzoic esters in absolute alcohol at 25° with N HCl.[8]
7. R. Acid catalyzed bromination of substituted acetophenones in an acetic acid–water–hydrochloric acid medium at 25°.[9]
8. R. Base catalyzed bromination of substituted acetophenones in acetic acid–water medium with sodium acetate as catalyst at 35°.[10]
9. E. Ionization of 2-furoic acids substituted in the 5-position, which was considered analogous to the para position in a benzene derivative.[11]
10. R. Alkaline hydrolysis of substituted benzamides in water at 100°.[12]
11. R. Acid hydrolysis of substituted benzamides in water at 100°.[12]
12. E. Ionization of substituted phenylboric acids in 25% ethyl alcohol at 25°.[13]
13. R. Reaction of substituted benzoyl chlorides with ethyl alcohol in alcohol medium at 0°.[14]
14. R. Reaction of substituted benzoyl chlorides with methyl alcohol at 0°.[15]
15. R. Reaction of substituted benzoyl chlorides with aniline in benzene at 25°.[16]
16. R. Reaction of substituted anilines with dinitrochloronaphthalene in ethyl alcohol at 25°.[17]
17. R. Reaction of substituted anilines with dinitrochlorobenzene in ethyl alcohol at 25°.[18]
18. R. Same as 17, but at 100°.[17]
19. R. Reaction of substituted dimethylanilines with methyl iodide in an acetone–water medium at 35°.[19]
20. R. Reaction of substituted phenyldiethylphosphines with ethyl iodide in acetone at 35°.[19]
21. R. Reaction of substituted dimethylanilines with trinitrophenol methyl ether in acetone at 35°.[20]
22. R. Reaction of substituted dimethylanilines with trinitrocresol methyl ether in acetone at 25°.[21]
23. R. Reaction of substituted anilines with benzoyl chloride in benzene at 25°.[16]
24. E. Formation of substituted formanilides from substituted anilines and formic acid in a pyridine–water medium at 100°.[22]
25. R. Reaction of substituted anilines with formic acid in pyridine–water medium at 100°.[23]
26. R. Hydrolysis of substituted formanilides, conditions same as in 25.[23]
27. R. Hydrolysis of substituted benzenesulfonic ethyl esters in 30% ethyl alcohol at 25°.[24]

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(5) Kindler, (a) *Ann.*, **450**, 1 (1926); (b) *ibid.*, **452**, 90 (1927); (c) *ibid.*, **464**, 278 (1928).

(6) (a) Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932); (b) Hall, *ibid.*, **52**, 5115 (1930); (c) Hammett and Paul, *ibid.*, **56**, 827 (1934); Farmer and Warth, *J. Chem. Soc.*, **85**, 1713 (1904).

(7) (a) Hantzsch and Farmer, *Ber.*, **32**, 3080 (1899); (b) Boyd, *J. Chem. Soc.*, **107**, 1538 (1915).

(8) Goldschmidt, *Ber.*, **28**, 3220 (1895).

(9) (a) Nathan and Watson, *J. Chem. Soc.*, 217 (1933); (b) Evans, Morgan and Watson, *ibid.*, 1167 (1935).

(10) Morgan and Watson, *ibid.*, 1173 (1935).

(11) Catlin, *C. A.*, **30**, 935 (1936).

(12) Reid, (a) *Am. Chem. J.*, **21**, 284 (1899); (b) *ibid.*, **24**, 397 (1900).

(13) Branch, Yabroff and Bettman, THIS JOURNAL, **56**, (a) 937, (b) 1850, (c) 1865 (1934).

(14) Norris, Fasce and Staud, *ibid.*, **57**, 1415 (1935).

(15) Norris and Young, *ibid.*, **57**, 1420 (1935).

(16) Williams and Hinshelwood, *J. Chem. Soc.*, 1079 (1934).

(17) Van Opstall, *Rec. trav. chim.*, **52**, 901 (1933).

(18) Singh and Peacock, *J. Phys. Chem.*, **40**, 669 (1936).

(19) Davies and Lewis, *J. Chem. Soc.*, 1599 (1934).

(20) Hertel and Dressel, *Z. physik. Chem.*, **B29**, 178 (1935).

(21) Hertel and Dressel, *ibid.*, **B23**, 281 (1934).

(22) Davis, *ibid.*, **78**, 353 (1911).

(23) Davis and Rixon, *J. Chem. Soc.*, **107**, 728 (1915).

(24) Demény, *Rec. trav. chim.*, **50**, 60 (1931).

TABLE III (*Concluded*)

28. R. Hydrolysis of substituted benzoyl chlorides in acetone–water medium at 0°.[25]
29. R. Friedel–Crafts reaction of substituted benzenesulfonyl chlorides with benzene at 30°.[26]
30. R. Reaction of substituted phenolate ions with ethylene oxide in 98% ethyl alcohol at 70.4°.[27]
31. R. Reaction of substituted phenolate ions with propylene oxide, conditions as in 30.[27]
32. R. Reaction of substituted phenolate ions with ethyl iodide in alcoholic solution at 42.5°.[28]
33. R. Acid catalyzed hydrolysis of substituted aryl sulfuric acids in water solution at 48.6°.[2]
34. R. Addition of hydrogen sulfide to substituted benzonitriles in alkaline alcoholic solution at 60.6°.[5a]
35. R. Alkaline hydrolysis of substituted phenylacetic esters, conditions as in 2.[5b]
36. E. Ionization of substituted phenylacetic acids in water at 25°.[3,29]
37. R. Hydrolysis of substituted benzyl chlorides in acetone–water medium at 69.8°.[30]
38. R. Reaction of substituted benzyl chlorides with potassium iodide in acetone at 20°.[30]
39. R. Reaction of substituted ald-chlorimines with sodium hydroxide in 92.5% alcohol at 0°.[31]

The deviations from equation (1) are undoubtedly larger than those to be expected from any reasonable error in the actual measurement of rate or equilibrium as Dippy and Watson[32] have pointed out in connection with reaction 2. It is by no means so certain that they do not in some cases result from insufficient purity of reactants. The preparation and proper purification of the numerous substituted compounds is by no means an easy task, even for a skilled organic chemist, a fact which is strongly emphasized by the discovery of Bennett and Jones[33] that the data in the previous literature on the reaction rate of substituted benzyl chlorides with iodide ion were in error by two orders of magnitude because of the presence of extremely reactive impurities. Another source of danger in the study of any organic reaction is the possibility that the product analyzed for may be produced by more than one reaction, as in the case noted by Baker,[34] or even that the same over-all reaction may result from either or both of two competing reactions which are differently affected by substituents. Thus the hydrolysis of a halide may proceed either by a reaction with water or by a reaction with hydroxyl ion.[35] It seems hardly likely that these difficulties should account for all of the deviations noted, but they may very well be responsible for some of the worst cases.

The errors show no tendency to be larger for reactions with a large value of ρ. Consequently the probable percentage error in the prediction of an equilibrium or rate constant from Tables I and II is no greater in the case of reactions in which a substituent produces a large change in constant than it is with reactions in which a substituent has very little effect. This rather distorts the effect one gets from a graphical test, as can be seen in Fig. 1, in which all four reactions have nearly the same value of r.

In most cases the distribution of errors for a given substituent is a random one. In a few cases, notably those of the fluorine derivatives, of *m*-methoxy derivatives and the naphthalene compounds, there are indications that a somewhat better choice of σ values could be made, but there are hardly enough data in any of these cases to justify such a refinement.

In one case only, that of the *p*-nitro substituent, it has been impossible to represent all reactions with one value of σ. Even here, however, it is not a question of a range of values but of two widely different ones. One of these, listed as *p*-NO_2(a) with a value of +1.27 in Table I gives satisfactory agreement with all reactions of aniline or phenol derivatives; the other, listed as *p*-NO_2(b) with the value +0.778, applies to the reactions of all other compounds.

In addition to providing a test of equation (2), Tables I and II perform the function of compressing into a small space a large amount of experimental data, and of providing the material for a wide variety of predictions of unknown equilibrium and rate constants.

The factor $1/d^2$ or some closely related function of the distance from substituent to reacting group is demanded by an important relationship noted by Kindler.[5b] This is to the effect that the quantity K/K^0 for the alkaline hydrolysis of a series of meta and para substituted cinnamic esters varies as the square root of the corresponding quantity for the similarly substituted benzoic esters. This relationship is shown in the lower

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[25] Olivier and Berger, *Rec. trav. chim.* **46**, 516 (1927).

[26] Olivier, *ibid.*, **33**, 244 (1914).

[27] Boyd and Marle, *J. Chem. Soc.*, **105**, 2117 (1914).

[28] Goldsworthy, *ibid.*, 1254 (1926).

[29] Dippy and Williams, *ibid.*, **161** (1934).

[30] Bennett and Jones, *ibid.*, 1815 (1935).

[31] Hauser, Le Maistre and Rainsford, THIS JOURNAL, **57**, 1056 (1935).

[32] Dippy and Watson, *J. Chem. Soc.*, 436 (1936).

[33] Bennett and Jones, *ibid.*, 1815 (1935).

[34] Baker, *ibid.*, 987 (1934).

[35] Olivier and Weber, *Rec. trav. chim.*, **53**, 869; 891 (1934).

plot in Fig. 2, in which the abscissa of each point is given by the logarithm of the hydrolysis rate constant of a substituted benzoic ester, and the ordinate by the constant for a cinnamic ester carrying the same substituent. The straight line is a plot of the equation, obtained by least squares methods.

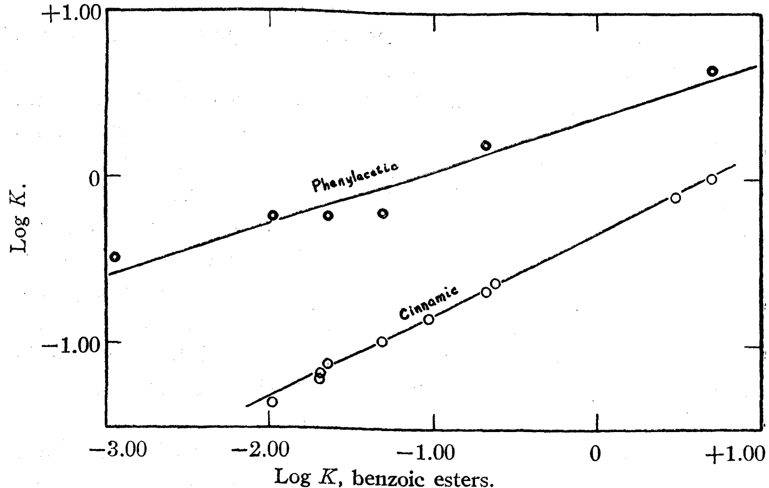

Fig. 2.—Relationships between hydrolysis constants.

$$\log K_c = -0.331 + 0.502 \log K_b \qquad (3)$$

and the median deviation or probable error of the points is only 0.014. The slope 0.502 agrees excellently with Kindler's relationship which requires a slope of 0.5 for the logarithmic plot.

If equation (1) applies to the hydrolysis constants of both sets of esters

$$-RT \ln K_c + RT \ln K_c^0 = \frac{A}{d_c^2}\left(\frac{B_1}{D} + B_2\right)$$

$$-RT \ln K_b + RT \ln K_b^0 = \frac{A}{d_b^2}\left(\frac{B_1}{D} + B_2\right)$$

it follows that

$$\log K_c = \text{constant} + (d_b/d_c)^2 \log K_b \qquad (4)$$

that is to say, equation (1) predicts a linear plot in Fig. 2 with a slope equal to $(d_b/d_c)^2$. If we estimate the value of d_b to be 5 Å. and that of d_c to be 7 Å., we obtain for the slope the value of 0.51 which is in satisfactory agreement with equation 3.

The agreement vanishes when, as in the upper plot in Fig. 2, Kindler's values for the hydrolysis constants of phenylacetic esters are plotted against the benzoic ester values. The median deviation of the points from the best straight line is 0.069, five times greater than in the cinnamic ester case, and the line has a slope of 0.325, smaller than the slope for the cinnamic esters, instead of larger, as would be expected. The scantier data available for hydrocinnamic esters suffice to show that the same complicating influence which appears in the phenylacetic case is present with these compounds also. It seems probable therefore that the simple relationship of equation (1) applies only when a continuous system of conjugated double bonds exists between substituent and reacting group.

The $1/D$ factor in equation (1) is in agreement with Wynne-Jones'[36] observation that, in the case of the ionization of organic acids, the quantity $\log K - \log K^0$ is linear in $1/D$, a relationship which applies to all organic acids, and not merely to those here under discussion. Data are not available for a test of the corresponding relationship on other reactions. It is a further corollary of the presence of this factor that a plot of the $\log K$ values obtained in a medium of dielectric constant D_1 against the values for the same reaction in a medium of dielectric constant D_2 should be linear with the slope $D_2(B_1 + B_2D_1)/D_1(B_1 + B_2D_2)$. The linearity is satisfactorily verified by comparison of the results of Wooten and Hammett[37] on ionization constants in butyl alcohol with the ionization constants of the same acids in water.[3] From data on eight substituents a slope of 1.48 with a median deviation of 0.025 is obtained. As was explained in a previous paper[38] the magnitude of the slope is not predictable because of the high salt concentration in the butyl alcohol experiments.

The effect of temperature upon the relative strengths of carboxylic acids has been discussed in a previous paper,[38] but the treatment needs minor modifications. In terms of equation (1) the quantity ΔF varies with temperature only because of the temperature dependence of the dielectric constant. Consequently ΔS, the difference between the entropies of reaction or of activation for the substituted and for the unsubstituted reactants, is given by

$$\Delta S = -\frac{\delta \Delta F}{\delta T} = \frac{AB_1}{d^2 D^2}\frac{\delta D}{\delta T}$$

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[36] Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

[37] Wooten and Hammett, THIS JOURNAL, **57**, 2289 (1935).

[38] Hammett, *J. Chem. Phys.*, **4**, 613 (1936).

If the constant B_2 is negligible, this becomes

$$\Delta S = \Delta F\, \delta \ln D/\delta T \qquad (6)$$

a result with which the available data on the ionization of meta and para substituted benzoic acids are in agreement.[38] The quantity $\delta \ln D/\delta T$ is in general negative in sign, is equal to -0.005 for the solvent water, and is of the same order of magnitude for many organic liquids. If, on the other hand, the quantity B_1 is negligible, ΔF should be independent of temperature. This is very nearly the case for the alkaline hydrolysis of esters, for which the work of Ingold and Nathan[39] leads to a mean value of the ratio $\Delta S/\Delta F$ equal to only 0.00028 ± 0.00007.

In any case there should be a direct proportionality between ΔS and the quantity $\delta \Delta F/\delta D$, the change in ΔF per unit change in dielectric constant, since

$$\Delta S = -\frac{\delta \Delta F}{\delta D}\frac{\delta D}{\delta T} \qquad (7)$$

The existence of this proportionality has been demonstrated for the ionization of benzoic acids, but data are not available for the comparison of observed and calculated values of the proportionality constant.[38]

The existence of the relationships embodied in equation (1) must to a considerable extent determine the nature of any theory which may be adopted to account for the effect of substituents upon rates and equilibria. The theory of a dipole field transmitted through the medium can, as previously indicated,[38] account for the observed dependence of ΔF for the ionization of benzoic acids upon dielectric constant and temperature, but fails by an order of magnitude to account for the actual values of ΔF in this reaction or for the fact that a given substituent may have a several times larger ΔF in other reactions. If the latter difficulty is avoided by the hypothesis that there is an internally transmitted effect as well as the one transmitted through the medium, it becomes necessary to admit that this additional effect is of an entirely different sort, and not merely an internally transmitted dipole field, because such a field could have no greater effect in the hydrolysis of a benzoic ester than in the ionization of benzoic acid. It then becomes quite inconceivable that the two effects should be linearly related in different reactions, as equation (2) demands, and especially that they should show so exactly the same dependence upon distance as Kindler's observations on the hydrolysis of cinnamic and benzoic esters demand. It is therefore an unavoidable conclusion that a substituent affects rates and equilibria essentially by a single internally transmitted mechanism.

The only reasonable theory of such an internal effect seems to be the one of an internal displacement of electrons which has been much discussed by Ingold[40] and to which Wheland and Pauling[41] have given a more definite mechanism and description in terms of quantum mechanical ideas. According to this theory a substituent alters the average density of electron charge in every part of the molecule. This may be either because the substituent directly attracts or repels electrons more than does the hydrogen atom it replaces, or because the substituent permits the construction of alternative electronic distributions of a highly polar nature which resonate with the non-polar one, or from some combination of these effects. In any case the altered concentration of electrons on the atom by which the substituted molecule enters into the reaction under consideration must alter both equilibrium and rate constant for the reaction because both depend upon an energy of bond formation which is itself a function of the electron density. Consider the reaction

$$XC_6H_4NH_2 + HA \rightleftharpoons XC_6H_4NH_3^+ + A^- \qquad (8)$$

by which aniline derivatives act as bases. When the reaction proceeds to the right a new bond between hydrogen and nitrogen is formed, which depends upon electrons originally present on the nitrogen. This bond will be more stable the greater the concentration of available electrons, consequently a substituent which increases the electron density on the nitrogen atom must increase the equilibrium constant of the reaction, that is to say, it must increase the basicity of the aniline.

The reaction rate problem is most satisfactorily treated in terms of the illuminating idea of Eyring[42] and of Evans and Polanyi[43] according to which the rate of a reaction is proportional to the concentration of a transition state of maximum energy, which concentration can be calculated by the same statistical mechanical methods as if there were reversible chemical equilibrium between reactants and transition state. In the reaction

$$XC_6H_4NH_2 + CH_3I \longrightarrow XC_6H_4NH_2CH_3^+ + I^- \qquad (9)$$

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[39] Ingold and Nathan, *J. Chem. Soc.*, 222 (1936).

[40] See for instance Ingold, *Chem. Rev.*, **15**, 225 (1934).

[41] Wheland and Pauling, THIS JOURNAL, **57**, 2086 (1935).

[42] Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

[43] Evans and Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

for instance the transition state is a half-reacted state in which the methyl group has not completely let loose from the iodide ion, but is already partly attached to the nitrogen atom by electrons whose source is the aniline molecule. Obviously the probability of such a transition state and hence the rate of reaction will be increased by a substituent which increases the density of electrons on the nitrogen atom.

Clearly this picture is qualitatively in agreement with the effect represented by the second term in equation (1), although it does not immediately suggest the simplicity of the actual relationship. The factor A measures the tendency of the substituent to displace electrons, the factor B_2/d^2 measures both the displaceability of the electrons on the reacting group and the dependence of the free energy of reaction or of activation upon the change in electron density.

The first term in equation (1), AB_1/d^2D, may be accounted for in terms of the energy of a charged body in a dielectric medium, $e^2/2Da$ where e is the charge and a the radius of the body. By far the greater part of this energy in the case of a substance like benzoate ion must derive from that portion of the charge which is concentrated on the carboxylic group. Any charge distributed over the benzene nucleus can contribute little to the energy because of the large dimensions of the structure over which it is distributed. A substituent like the nitro group which attracts electrons must draw some of the charge off the carboxylic group, and even though this charge is again concentrated on a small structure, the nitro group, the electrostatic energy must decrease, because the effect depends upon the square of the charge. Thus if the energy due to the charge on the CO_2^- group in benzoate ion is given by $e^2/2Da$ and if the NO_2 group shares the charge equally with the CO_2^- in nitrobenzoate ion, the energy of the latter becomes

$$2(e/2)^2/2Da = 1/2(e^2/2Da)$$

which is one-half as great as the energy of the benzoate ion. This effect alone would make the free energy change negative in the reaction

$$NO_2C_6H_4CO_2H + C_6H_5CO_2^- \rightleftharpoons NO_2C_6H_4CO_2^- + C_6H_5CO_2H \quad (10)$$

and increase the equilibrium constant above unity. An additional favorable factor is the fact that the wave function for nitrobenzoic acid must contain a considerable contribution from a dipolar configuration with a negative charge on the NO_2 group and a positive charge on the CO_2H, whose electrostatic energy would also contribute to increasing the energy of the left-hand side of equation (10). Both of these energy changes will have a magnitude proportional to $1/D$, in agreement with equation (1).

Since the quantities B_1 and B_2 depend upon quite different phenomena, they are independently variable from reaction to reaction, and may even differ in sign. This is the case in the hydrolysis of aryl sulfuric acids (reaction 33) studied by Burkhardt, Ford and Singleton.[2] Here the mean value of the ratio $\Delta S/\Delta F$ is found to be 0.0035 ± 0.0001, and from equations (1) and (5) we have, using $\delta \ln D/\delta T = -0.005$

$$AB_1/d^2D = -0.7\Delta F$$
$$AB_2/d^2 = 1.7\Delta F$$

B_1 presumably will have its largest values when reactants, products or transition state contain electrically charged molecular species, it need not however be zero in the absence of these because of the possible presence of dipoles with widely separated charges. The sensitivity to structure of reactants exhibited by ρ of equation (2), which represents the total effect of the B_1 and B_2 terms is surprisingly large. Thus the value of ρ for reaction 30, the reaction of a series of substituted phenolate ions with ethylene oxide is -0.946, while the value for the reaction of the same substances with propylene oxide (reaction 31) is -0.771.

The relationships contained in equation (1) are applicable only to meta and para substituted benzene derivatives; the situation is more complicated both with ortho substituted benzene derivatives and with aliphatic or mixed aromatic-aliphatic compounds. A substituent in the ortho position to the reacting group exerts an influence upon both equilibrium and rate of reaction, which is frequently but not always of great magnitude, and whose governing laws and mechanism are evidently entirely different from those concerned in the effect of more distant substituents.[1,5,22,44,45] One corollary only of equation (1) remains valid in the case of an ortho substituent, namely, that represented by equation (7).[38] Consequently the temperature effect upon ΔF may be described as the result of the temperature dependence of the dielectric constant even in the case of an ortho substituent.

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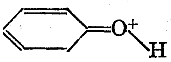
[44] Schwarzenbach and Egli, *Helv. Chim. Acta*, **17**, 1184 (1934).

[45] Hammett and Pfluger, THIS JOURNAL, **55**, 4079 (1933).

In the case of aliphatic compounds equation (7) also fails, even as the crudest approximation.[38] It seems probable that in this case factors appear in the partition functions whose ratio determines the value of ΔF which are dependent upon the internal motions of the reacting molecules and which fail to cancel out between numerator and denominator. As a result the free energy change is not equal to the difference in potential energy between products and reactants and is dependent upon temperature.[38] On this basis the applicability of equation (1) is dependent upon a rigidity of structure which is indeed inherent in most of the reactants to which we have applied the equation, and whose absence in other cases results in some of the most striking failures of the equation.

Pauling[46] has recently pointed out that the freedom of rotation of any side chain attached to the benzene ring is limited or destroyed whenever the classical formula with a single link between side chain and ring resonates with another configuration with a double link in the same position. Thus the actual structure of phenol partakes sufficiently of such structures as



to prevent rotation around the carbon-oxygen link. The same effect must exist in the various derivatives of phenol, aniline and benzoic acid which we have considered, and it should notably ossify the structure of cinnamic ester and its derivatives, but not those of the phenylacetic and hydrocinnamic esters. The striking contrast shown in Fig. 2 between the exact correlation of the hydrolysis rates of cinnamic esters with those of benzoic esters, and the poor correlation of the rates for phenylacetic esters is therefore entirely in agreement with this hypothesis.

Since the benzyl halides are incapable of this kind of resonance, there should be free rotation of the side chain. In agreement with this prediction we find very poor correlation between our σ constants and the reaction rates of benzyl halides. This is notably true for the hydrolysis (reaction 37) for which $r = 0.15$, but the reaction with iodide (reaction 38) has an r greater than the average, and a direct comparison of the iodide reaction with the hydrolysis gives a very poor correlation, the probable error in log K for the hydrolysis predicted from the iodide reaction being 0.20. On the other hand, there is excellent correlation between hydrolysis rate and rate of reaction with a tertiary amine.[47]

Clearly, then, linear logarithmic relationships between equilibrium or rate constants of different reactions are not limited to cases to which equation (1) is directly applicable. This fact appears indeed in the prototype of all such relationships, the relation between acid or base strength and catalytic effect discovered by Brönsted and Pedersen.[48] This applies both to aliphatic and aromatic acids, to ortho substituted as well as to meta and para substituted compounds. The same thing is true of Hammett and Pfluger's[45] relationship between the rate of alkylation of an amine by the methyl ester of an acid and the strength of the acid. Evidently the factors which cause the deviations from equation (1) may have linearly related effects upon two different reactions, provided these reactions are sufficiently closely related. Yet even in the case of general basic catalysis, Pfluger[49] has found significant deviations from a straight line plot when the alterations in structure take place in the reacting group itself as when diethylaniline is substituted for dimethylaniline.

Summary

A simple formula is proposed to represent the effect of a substituent in the meta or para position of the benzene ring upon the rate or equilibrium of a reaction in which the reacting group is in a side chain attached to the ring. This formula represents not only the total effect of the substituent but also the influence of changing length of side chain, of dielectric constant of the medium, and of temperature within a satisfactory precision in a wide variety of cases. The theory that a substituent acts by internal electron displacement is in complete agreement with this formula, including the temperature and medium effects embodied in it, and accounts also for the large deviations observed in the case of non-rigid structures.

A table of substituent constants and one of reaction constants has been calculated from which the effect of many substituents upon a large number of reaction rates and equilibria may be obtained by multiplication of the constants.

NEW YORK, N. Y. RECEIVED NOVEMBER 7, 1936

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[46] Pauling, THIS JOURNAL, 58, 94 (1936).

[47] See Fig. 9 of ref. 1.

[48] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[49] Unpublished results kindly communicated to me by Dr. H. L. Pfluger.

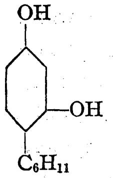
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

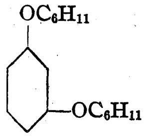
The Pentenyl-, Hexenyl- and Heptenylresorcinols

BY CHARLES D. HURD AND RAYMOND W. MCNAMEE[1]

Hexylresorcinol has been studied considerably in recent years but no attention has been given to its unsaturated analogs. The allylresorcinols[2] are the only alkenylresorcinols to have been investigated although the hexenyl- and heptenylpyrogallols have been described recently.[3]

In the synthesis of 4-hexenylresorcinol (A), 1-bromo-2-hexene was reacted with resorcinol and potassium carbonate in acetone solution. Concurrently, there was formed resorcinol hexenyl diether (B), which was separated by insolubility in alkali, and 4,6-dihexenylresorcinol (C) which was separated from (A) by its lower volatility. The pentenyl- and heptenylresorcinols were prepared analogously. A molecular still was advantageous for the distillation of these substances. The alkenylresorcinols were characterized by solid derivatives (D) with chloroacetic acid. The methyl diethers (E) were also synthesized.


(A)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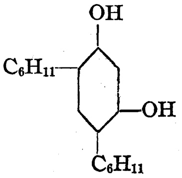
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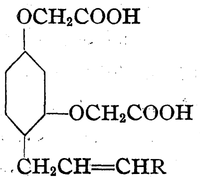
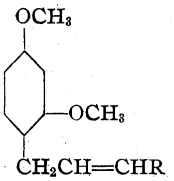
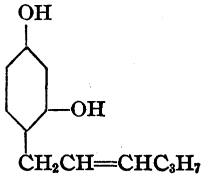
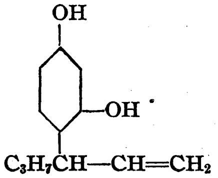

(D)

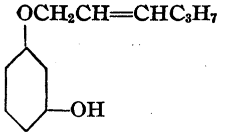

(E)

The structure of the alkenyl group in these compounds is a matter of some interest. Obviously, it is related to the structure of the alkenyl bromide used in the synthesis. Instead of regarding this as pure 1-bromo-2-alkene as has been done in the past,[4] it should be regarded as an equilibrium mixture of 1-bromo-2-alkene and 3-bromo-1-alkene, the former predominating. This aligns the structure with that of "crotyl" bromide, which has been proved[5] to be an equilibrium mixture of 1-bromo-2-butene and 3-bromo-1-butene, with the former in considerable excess.

On this basis, (A) should be regarded as a mixture of F + G. It is reasonably certain that (A) was formed from resorcinol by direct substitution. Therefore, the F:G ratio should approximate the ratio of the two substances in hexenyl bromide. Hydrogenation of the (F + G) mixture yielded a mixture of hexylresorcinols from which *n*-hexylresorcinol crystallized.


(F)


(G)


(H)

Structure (G) might be regarded as coming from the ether (H) by pyrolysis. On heating, (H) should rearrange into (G) but temperatures of 200–220° would be required whereas 100° was the maximum temperature in this work. Both (B) and (H)[6] have been shown to be stable at 100°.

The position of the hexenyl group in hexenylresorcinol was established by oxidizing the methyl diether (E) to 2,4-dimethylbenzoic acid.

Bactericidal data on the resorcinol derivatives were obtained through the courtesy of the Parke, Davis and Company Laboratories. The phenol coefficients toward three test organisms are listed in Table I. The values of two related compounds are included for comparison.

Experimental Part

Reagents.—The syntheses of 1-bromo-2-hexene and 1-bromo-1-heptene have been described.[3] That for 1-bromo-2-pentene was as follows. 1-Pentene-3-ol, b. p. 35–37° (20 mm.), was prepared in 78% yield by dropping a solution of acrolein in ether into an excess of ethylmagnesium bromide at −5°. Then a mixture of 121 g. of this alcohol, 350 g. of 48% hydrobromic acid and 100 g. of concd. sulfuric acid was stirred for twenty-four hours.

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[1] Parke, Davis and Company Fellow, 1931–1933.

[2] Hurd, Greengard and Pilgrim, THIS JOURNAL, **52**, 1700 (1930).

[3] Hurd and Parrish, *ibid.*, **57**, 1731 (1935).

[4] Bouis, *Ann. chim.*, [10] **9**, 421 (1928).

[5] Winstein and Young, THIS JOURNAL, **58**, 104 (1936).

[6] Hurd and Schmerling, *ibid.*, **59**, 107 (1937).

TABLE I

PHENOL COEFFICIENTS

	Test organism		
Compound	*Staph. aureus* at 37.5°	*Strep. hemol.* at 37.5°	*B. typhosus* at 20.5°
Phenol	1	1	1
4-*n*-Hexylresorcinol[a]	98	...	56
Resorcinol *n*-hexyl monoether[a]	125	...	46
4-Hexenylresorcinol	150	200	40
4,6-Dihexenylresorcinol	>200	>200	>30
Mixture of 4-hexyl-resorcinol and isomers	150	125	..
4-Pentenylresorcinol	20	...	..

[a] Klarmann, Gatyas and Shternov, THIS JOURNAL, **53**, 3402 (1931). The temperature was 37°.

After dilution with water, the pentenyl bromide layer was separated, washed, dried and distilled. It boiled at 38–41° (19 mm.); n^{21}D 1.4757. The yield was 169 g. or 80%. It was chiefly 1-bromo-2-pentene but was probably in equilibrium with 3-bromo-1-pentene.

The Alkenylresorcinols

4-Hexenylresorcinol.—Forty-nine grams (0.3 mole) of 1-bromo-2-hexene was added during three hours to a well-stirred mixture of 66 g. of resorcinol (0.6 mole), 300 cc. of acetone and 40 g. of anhydrous potassium carbonate. The mixture was then refluxed for three hours. The acetone was removed by distillation and the residue was extracted with carbon tetrachloride. The resulting solution was washed free of resorcinol by many extractions with water. The alkali-soluble material was then separated from the mixture by use of a dilute solution of sodium hydroxide.

The alkaline solution was acidified with hydrochloric acid and the solution was extracted with ether. The extract was washed with water, dried and distilled from a Hickman molecular still[3] (p. 1732) at 0.003–0.005 mm. The bottom of the still was heated by a steam-bath. Thirty grams of distillate accumulated. It was redistilled. The first 23 cc. to come over (collected in several fractions) possessed a uniform index of refraction, n^{25}D 1.5388. That for the next 7 cc. was 1.5416. The 23-cc. portion, d^{25}_4 1.0481, was hexenylresorcinol.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.0; H, 8.32. Found: C, 74.5; H, 8.32.

4-Pentenylresorcinol.—This was prepared similarly from 66 g. of resorcinol, 45 g. of 1-bromo-2-pentene, 40 g. of potassium carbonate and 300 cc. of acetone. Several arbitrary fractions were collected in the Hickman still and the index of refraction taken. Those of similar constants were combined and refractionated thrice. In this way, 7 g. of pentenylresorcinol, n^{25}D 1.5461, d^{25}_4 1.0671, was obtained.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.92. Found: C, 73.9; H, 7.99.

4-Heptenylresorcinol.—The general details were similar, these quantities of reagents being used: 85.5 g. of 1-bromo-2-heptene (0.5 mole), 110 g. of resorcinol (1 mole), 60 g. of potassium carbonate and one liter of acetone. The preliminary fractionation was by vacuum distillation at 1 mm. There was 17 cc. at 138–143°, 11 cc. at 143–150°, 7 cc. at 150–170° and 3.5 cc. of residue. The 17-cc. fraction contained the bulk of the heptenylresorcinol, and the 7-cc. fraction contained some diheptenylresorcinol (see below). Subsequent fractionations were performed in the Hickman still (at 100°) and 14 cc. of product, n^{25}D 1.5360, was obtained.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 75.7; H, 8.80. Found: C, 75.5; H, 8.79.

The Diethers

Resorcinol Hexenyl Diether, $C_6H_4(OC_6H_{11})_2$.—The carbon tetrachloride solution from which 4-hexenylresorcinol had been extracted was distilled in a Hickman still at 100° after it was washed free of alkali and dried. Seven grams of a mobile liquid was obtained, n^{25}D 1.5172, d^{25}_4 0.9634.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.48. Found: C, 78.4; H, 9.50.

Resorcinol Pentenyl Diether.—This diether was obtained similarly from the carbon tetrachloride solution from which 4-pentenylresorcinol had been extracted. The distillate from the Hickman still weighed 3.5 g.; n^{25}D 1.5227, d^{25}_4 0.973.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.0; H, 9.01. Found: C, 78.3; H, 9.01.

Chloroacetic Derivatives of the 4-Alkenylresorcinols

2,4-Di-(carboxymethoxy)-1-hexenylbenzene (Structure D).—One gram of 4-hexenylresorcinol, 3.5 g. of chloroacetic acid and an excess of 10% sodium hydroxide solution were heated on a steam-bath for an hour. The solution was cooled, acidified and extracted with ether. The extract was washed with water and extracted with a solution of sodium bicarbonate. On acidification of the bicarbonate extract, the desired acid precipitated. After several crystallizations from 50% methanol it melted at 159–160°; yield 0.5 g.

Anal. Calcd. neut. equiv. for $C_6H_{11}C_6H_3(OCH_2COOH)_2$, 154. Found: 157.

2,4 - Di - (carboxymethoxy) - 1 - pentenylbenzene.—The m. p. of this derivative, prepared similarly from 4-pentenylresorcinol, was 164–165°.

Anal. Calcd. neut. equiv. for $C_5H_9C_6H_3(OCH_2COOH)_2$, 147. Found: 150.

2,4 - Di - (carboxymethoxy) - 1 - heptenylbenzene.—This acid, similarly prepared, melted at 144–145°.

Anal. Calcd. neut. equiv. for $C_7H_{13}C_6H_3(OCH_2COOH)_2$, 161. Found: 162.

Hydrogenation of the Hexenylresorcinol.—Four grams of 4-hexenylresorcinol was hydrogenated catalytically using 0.15 g. of the Adams platinum oxide catalyst, 200 cc. of ethyl alcohol, and hydrogen. The hydrogenation took an hour, but most of the hydrogen was absorbed in the first fifteen minutes. After filtration, the material was distilled at 3 mm. Two cc. of distillate (b. p. 130–135°, n^{25}D 1.5320, d^{25}_4 1.056) remained as an oil, but 0.6 cc. (b. p. 135–140°) solidified on standing. The latter melted at 67–68° which is the m. p. of 4-hexylresorcinol.[7] The 2-cc. fraction also analyzed correctly for hexylresorcinol but the fact that it would not crystallize, even

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(7) Dohme, Cox and Miller, THIS JOURNAL, **48**, 1688 (1926).

when seeded, indicated that the material was a mixture of *n*-hexylresorcinol and isomers, presumably 4-(α-ethylbutyl)-resorcinol and resorcinol *n*-hexyl monoether (formed via the hexenyl monoether). The phenol coefficient of this fraction was determined (Table I).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.28. Found: C, 74.1; H, 9.33.

Methylation of the Alkenylresorcinols

4-Hexenylresorcinol Methyl Diether, $C_6H_{11}C_6H_3(OCH_3)_2$.—A mixture of 4.5 g. of 4-hexenylresorcinol, 50 cc. of 10% sodium hydroxide solution and 20 g. of methyl sulfate was stirred vigorously for an hour. The insoluble layer was drawn off, the aqueous layer was extracted with ether and the combined insoluble layers were washed with water, dried and distilled in a Hickman still at 100° and 0.12–0.15 mm.; yield 4.5 g. When redistilled at 10 mm. the material boiled at 150–152°; $n^{7}\mathrm{D}$ 1.5233, $n^{25}\mathrm{D}$ 1.5154, $d^{25}{}_4$ 0.9865.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.4; H, 9.09. Found: C, 76.3; H, 9.02.

4-Pentenylresorcinol Methyl Diether.—4-Pentenylresorcinol (2.7 g.) was dissolved in 35 cc. of 10% sodium hydroxide solution and an excess of methyl sulfate was added. The mixture was stirred for one hour. The methylated compound was separated and distilled in a Hickman still. At 0.0005 mm. and 100° the material distilled at the rate of 20–25 drops per minute. The yield was 2.5 g.; $n^{25}\mathrm{D}$ 1.5192, $d^{25}{}_4$ 0.986.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.79. Found: C, 75.6; H, 8.72.

Oxidation to 2,4-Dimethoxybenzoic Acid.—Twenty grams of powdered potassium permanganate was added to a solution of 4.0 g. of 4-hexenylresorcinol methyl diether in 200 cc. of acetone (distilled from potassium permanganate). The mixture was heated on the water-bath and stirred mechanically. At the end of one hour the manganese dioxide was removed by filtration, 100 cc. of water was added and the acetone was removed by distillation. The solution became cloudy due to the precipitation of unoxidized material. This (0.35 g.) was removed by ether extraction. The water solution was made slightly acid with sulfuric acid and 1.3 g. of 2,4-dimethoxybenzoic acid[8] precipitated; m. p. after one crystallization, 108°.

4,6-Dihexenylresorcinol (Structure C).—Resorcinol (55 g., 0.5 mole) was added to a solution of sodium (6.9 g., 0.3 mole) in 400 cc. of absolute alcohol. Then, during two hours, 49 g. (0.3 mole) of 1-bromo-2-hexene was dropped into the stirred mixture. It was stirred for ten hours more and then refluxed for two hours. The solvent was distilled off, the residue extracted with carbon tetrachloride (100 cc.) and the extract washed repeatedly with water until free of resorcinol. It was dried and distilled at 3 mm. Forty grams was collected at 135–155°; residue, 4 g. It was redistilled at 3 mm. through a 15-cm. column, whereupon 25 g. of monohexenyl derivatives were removed in the first fractions. Then, 7.5 g. of dihexenylresorcinol was collected at 155–180°. The latter was redistilled in a Hickman still. The fraction thus obtained was analyzed; $n^{25}\mathrm{D}$ 1.5310, $d^{25}{}_4$ 0.9971.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.82; H, 9.48. Found: C, 79.07; H, 9.46.

This compound was also prepared in work with Mr. Louis Schmerling as follows. A suspension was made of sodium resorcinolate (from 5.5 g. of resorcinol and 2.3 g. of sodium) in benzene (25 g.). Eight grams of 1-bromo-2-hexene in 35 cc. of benzene was added and the mixture stirred for ten hours. Then another 8 g. was added and the mixture refluxed for nine hours. The benzene solution was decanted from the sodium bromide and washed repeatedly with water. After evaporation of the benzene under diminished pressure the residue was treated with 175 cc. of Claisen's aqueous–alcoholic potash (a mixture of 53 g. of potassium hydroxide and 44 cc. of water, made up to 175 cc. with methanol). A 2-g. fraction of resorcinol hexenyl diether was separated.

The alkaline solution was acidified with dilute sulfuric acid. The resulting oil was ether extracted, washed, dried and distilled in a Hickman still at 100°. About 2 g. of hexenylresorcinol was collected first, then 3.5 g. of dihexenylresorcinol (mol. wt., 265; calcd. for $C_{18}H_{26}O_2$, 274).

4,6-Dihexenylresorcinol Methyl Diether, $(C_6H_{11})_2C_6H_2(OCH_3)_2$.—The dihexenylresorcinol (3.5 g.) was dissolved in 10% sodium hydroxide solution after which it was stirred for an hour with an excess of methyl sulfate. The oil which separated was taken up in ether, washed, dried and distilled. Three grams of the diether was obtained; b. p. 158–163° at 10 mm., $n^{25}\mathrm{D}$ 1.5145, $d^{25}{}_4$ 0.957.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.4; H, 9.93. Found: C, 78.8; H, 10.0.

4,6-Diheptenylresorcinol, $(C_7H_{13})_2C_6H_2(OH)_2$.—This was a high-boiling by-product in the preparation of 4-heptenylresorcinol (see above). Its low volatility was witnessed by its slow rate of distillation from the Hickman still, namely, about one drop per minute at 100° and 0.0005 mm. Thus, from the less-volatile fractions there was finally obtained 2.5 cc. of oil which appeared to be 4,6-diheptenylresorcinol, $n^{25}\mathrm{D}$ 1.5265.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.4; H, 9.93. Found: C, 79.1; H, 10.1.

Summary

This paper describes the preparation of hexenylresorcinol, pentenylresorcinol and heptenylresorcinol by direct substitution of resorcinol with the corresponding alkenyl bromide. Concurrent reaction products were the dialkenylresorcinols and the resorcinol alkenyl diethers. The use of a molecular still greatly facilitated the separation and purification of these compounds. Chloroacetic acid derivatives and methyl ethers of the alkenylresorcinols were prepared.

From the hexenylresorcinol some *n*-hexylresorcinol was prepared by hydrogenation. Oxidation of hexenylresorcinol methyl diether gave rise to 2,4-dimethoxybenzoic acid.

Bactericidal data are included.

EVANSTON, ILL.

RECEIVED SEPTEMBER 21, 1936

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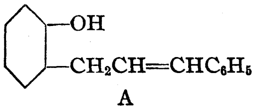
(8) Mauthner, *J. prakt. Chem.*, **210**, 43 (1921).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

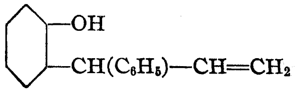
Observations on the Rearrangement of Allyl Aryl Ethers

BY CHARLES D. HURD AND LOUIS SCHMERLING[1]

In studying the cinnamyl derivatives of phenol, Claisen[2] found that the *o*-cinnamylphenol obtained by direct alkylation was different from the product obtained by pyrolysis of cinnamyl phenyl ether. To the former he assigned structure (A) and to the latter (B). Although this conclusion is not doubted from a qualitative standpoint, it has never been established whether or not (B) was formed exclusively or whether it was admixed to a small extent with (A). Since this is a matter of considerable importance in regard to the mechanism of rearrangement of allyl aryl ethers, it was decided to study this and other related questions.



A



B

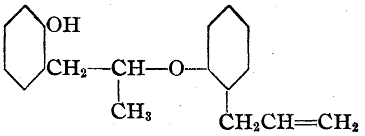
Accordingly, Claisen's two compounds were synthesized and subjected to ozonolysis. The ozonide from (A) should yield benzaldehyde but no formaldehyde on hydrolysis, whereas that from (B) should yield formaldehyde and no benzaldehyde. This was found to be the case, thus confirming Claisen's conclusion.

To determine whether the allyl aryl ether rearrangement is intra- or intermolecular, a mixture of cinnamyl phenyl ether, $C_6H_5—O—CH_2CH═CHC_6H_5$, and allyl β-naphthyl ether, $C_{10}H_7—O—CH_2CH═CH_2$ was heated. If intermolecular, some *o*-allylphenol should be formed. Since this is relatively low boiling (104° at 14 mm.) compared to 1-allyl-2-naphthol (177° at 12 mm.) or *o*-(α-phenylallyl)-phenol (190° at 13 mm.), its isolation from the reaction mixture would be accomplished easily. 1-Allyl-2-naphthol and *o*-(α-phenylallyl)-phenol were found but no *o*-allylphenol.

Similar evidence for the intramolecular nature of this rearrangement was obtained by studying a mixture of allyl β-naphthyl ether and 2-hexenyl phenyl ether.

In connection with this work, some of the hexenylresorcinols were synthesized. Resorcinol hexenyl monoether, $HOC_6H_4OCH_2CH═CHC_3H_7$, was isolated for the first time. It was insoluble in alkali and was stable at 100°.

The rearrangement of allyl phenyl ether into *o*-allylphenol was also studied. Claisen[3] obtained an 80% yield on heating at the reflux temperature for six hours. Our yields were only about half. The bulk of the product was a polymer from which a dimer and trimer were separated by distilling the tar from a molecular still. The dimer was soluble in dilute alkali, was unsaturated toward bromine, was unaffected[4] by hot formic acid, and had a molecular refraction of 80.5. These data are in harmony with *o*-(2-(*o*-allylphenoxy)-propyl)-phenol



which has a calculated molecular refraction of 81.1.

Experimental Part

Cinnamyl Phenyl Ether.—A mixture of cinnamyl bromide (80 g.), acetone (200 cc.), phenol (50 g.) and potassium carbonate (75 g.) was refluxed for four hours, then 200 cc. of water was added. The ether separated and solidified. It was washed with dilute alkali and water, and the yield was 78 g. or 92%. It melted at 67°. This is preferable to Claisen and Tietze's[5] method wherein sodium phenoxide reacted with cinnamyl bromide in methanol.

***o*-(α-Phenylallyl)-phenol.**—The rearrangement of cinnamyl phenyl ether by refluxing for four hours in diethylaniline was performed essentially as described by Claisen and Tietze. The reaction product boiled at 186–189° (18 mm.); phenylurethan, m. p. 93–94° (Claisen and Tietze reported 91°).

o-Cinnamylphenol (m. p. 55°, phenylurethan, m. p. 132°) was prepared according to Claisen's directions.[6] The essential feature of this synthesis was the gradual addition of cinnamyl bromide in benzene to a suspension of an equivalent quantity of sodium phenoxide in benzene followed by refluxing for five hours. Likewise, Claisen's directions[7] were followed in the preparation of allyl β-naphthyl ether, namely, the heating of a mixture of 0.1 molar quantities of β-naphthol, allyl bromide and potassium carbonate in 200 cc. of acetone. The refractive index at 25° was found to be 1.600. The synthesis of hexenyl phenyl ether (from 0.1 molar quantities of 1-bromo-2-

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[1] Parke, Davis and Company Fellow, 1933–1935.

[2] Claisen, *Ber.*, **58**, 279 (1925).

[3] Claisen, *Ann.*, **418**, 79 (1919).

[4] Semmler, *Ber.*, **41**, 2185 (1908) found that this is characteristic of compounds with allyl side-chains, whereas those with propenyl side-chains are resinified [to dimers, Glichtich, *Bull. soc. chim.*, **35**, 1160 (1924)].

[5] Claisen and Tietze, *Ber.*, **58**, 279 (1925).

[6] Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 234 (1925).

[7] Claisen, *Ber.*, **45**, 3158 (1912).

hexene, phenol, potassium carbonate and 200 cc. of acetone) and its pyrolysis to *o*-(α-*n*-propylallyl)-phenol followed the directions of Hurd and McNamee.[8]

Pyrolysis of Mixtures of Ethers.—A mixture of 7.5 g. of allyl β-naphthyl ether and 4.5 g. of cinnamyl phenyl ether was heated under a reflux condenser for four hours by a bath at 240°. An exothermic rearrangement was observed. The volume of the alkali-soluble portion was 3 cc. The only low-boiling material collected during distillation at 15 mm. was one drop of phenol. There was no evidence for *o*-allylphenol. One cc. of 1-allyl-2-naphthol was collected at 160–180°; n^{20}D 1.6170. It solidified on seeding with a crystal of 1-allyl-2-naphthol. At 180–190° there was obtained about 0.3 cc. of *o*-(phenylallyl)-phenol.

A mixture of 4.2 g. of allyl β-naphthyl ether and 4 g. of 2-hexenyl phenyl ether was heated similarly for six hours at a bath temperature of 250°. An exothermic reaction was noticed at 224° (temperature of mixture itself).

On working up the product (by alkali extraction and vacuum distillation) there was obtained 0.4 cc. of phenol which solidified and melted at 30°; bromination yielded tribromophenol, m. p. 96°. About 0.5 cc. of *o*-hexenylphenol, n^{22}D 1.5250, was collected at 128–148° (18 mm.), and 1.1 cc. of 1-allyl-2-naphthol, n^{16}D 1.6167, at 165–180°. The latter solidified. After crystallization from 50% alcohol it melted at 55°. No *o*-allylphenol, b. p. 104 (14 mm.), was observed.

Ozonolysis of *o*-Cinnamylphenol and *o*-(α-Phenylallyl)-phenol.—A 3% ozone stream was conducted through a solution of 3 g. of *o*-cinnamylphenol in 100 cc. of carbon tetrachloride for four hours. Some of the ozonide separated but the bulk of it was soluble. The solvent was removed under reduced pressure and the residual ozonide hydrolyzed with water. The aqueous layer (even on boiling) was free from any odor of formaldehyde. Also, formaldehyde was proved absent by the resorcinol ring test. The water-insoluble oil was taken up in ether, washed with dilute sodium bicarbonate and dilute sodium carbonate and evaporated. The residual benzaldehyde weighed 0.75 g.; its phenylhydrazone melted correctly at 155°.

Four grams of the isomeric *o*-(α-phenylallyl)-phenol, ozonized as before, yielded an oily ozonide which was hydrolyzed by shaking it with water and zinc dust. Formaldehyde was present in quantity as indicated by the strong odor and by the resorcinol ring test. The viscous, insoluble oil was taken up in ether and washed with sodium bicarbonate solution. Acidification of the wash solution gave no water-insoluble (benzoic) acid. The ether layer was then washed with sodium carbonate solution before evaporating the ether. The residue, a thick oil, gave no phenylhydrazone and yielded no benzoic acid on oxidation with potassium permanganate.

Resorcinol 2-Hexenyl Monoether.—Resorcinol (16.5 g.) was converted to its sodium salt by interaction with the calculated amount of sodium ethoxide in 400 cc. of absolute alcohol. This solution was added with stirring during three hours into 49 g. of 1-bromo-2-hexene. Stirring was continued overnight and then the solution was refluxed for two hours. The alcohol was removed and the residue extracted with carbon tetrachloride (125 cc.). The extract was washed with water to remove unreacted resorcinol. Then the solution was extracted with a 10% solution of sodium hydroxide. This process removed hexenylresorcinol but did not dissolve resorcinol hexenyl monoether or diether. From the alkaline extract by acidification, ether extraction and distillation in a Hickman still[9] at 100° and 0.001 mm. was obtained 6 cc. of 4-hexenylresorcinol,[10] n^{22}D 1.5398.

Anal. (Zerewitinoff) Calcd. for C_6H_{11}-$C_6H_3(OH)_2$: OH, 2.00. Found: OH, 1.99.

The alkali-insoluble portion was freed from the carbon tetrachloride and distilled in the Hickman still (100°, 0.001 mm.). Five fractions totaling 12.5 cc. were collected, all possessing nearly identical n^{23}D values of 1.5210. All five fractions were alkali-insoluble. Analysis proved this material to be resorcinol hexenyl monoether.

Anal. (Zerewitinoff) Calcd. for HO-C_6H_4-OC_6H_{11}: OH, 1.00. Found: OH, 1.00, 0.97.

The residue in the Hickman still contained resorcinol hexenyl diether. It was volatilized by raising the temperature of the still to 160° with an air-bath. Five grams of the diether[10] was collected, n^{23}D 1.5160.

Polymers of *o*-Allylphenol.—Allyl phenyl ether, b. p. 112–113° (34 mm.), n^{21}D 1.5208, n^{26}D 1.5190, was prepared in 82% yields according to Claisen's[11] directions. This ether (67 g.) was heated by a bath at 210–240° to maintain refluxing for five and a half hours. The temperature of the liquid rose from 190 to 220°. On working it up according to Claisen's directions there was obtained 23 g. of *o*-allylphenol (a 42% yield), and 3 g. of α-methylcumarane. A considerable quantity of dark, viscous tar remained in the distilling flask.

This tar was distilled from a Hickman still at 0.01 mm. With a bath temperature of 145° two 1-cc. fractions were collected which appeared to be a mixture of diallylphenol[12] and triallylphenol. The bath temperature was then raised to 245°, whereupon 10.5 cc. of an apparently uniform product, the dimer, distilled. The next 0.5-cc. fraction, collected at a bath temperature of 270°, set to a clear amber glass on cooling. Its molecular weight (calcd. for $C_{27}H_{30}O_3$, 402; found, 384) indicated that it was chiefly the trimer of *o*-allylphenol.

Properties of the Dimer.—The dimer was a liquid, n^{21}D 1.5825, d^{25}_{25} 1.11, easily soluble in 10% sodium hydroxide but almost insoluble in 20% alkali. The acetyl and benzoyl derivatives were oils. The substance absorbed bromine (in carbon tetrachloride) without the evolution of hydrogen bromide, and it was unaffected when heated with concentrated formic acid.[13] The molecular weight, determined cryoscopically in benzene, was satisfactory for the dimer.

Mol. wt. Calcd. for $C_{18}H_{20}O_2$, 268. Found: mol. wt., 270.

Summary

It was established by ozonolysis that the product of rearrangement of cinnamyl phenyl ether is

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[8] Hurd and McNamee, THIS JOURNAL, **54**, 1648 (1932).

[9] For set-up, see Hurd and Parrish, *ibid.*, **57**, 1732 (1935).

[10] Hurd and McNamee, *ibid.*, **59**, 104 (1937).

[11] Claisen, *Ann.*, **418**, 78 (1919).

[12] Similar findings have been established in unpublished work with W. A. Yarnall.

[13] Semmler, *Ber.*, **41**, 2185 (1908).

o-(*α*-phenylallyl)-phenol, unadmixed with any *o*-cinnamylphenol. Similarly, *o*-cinnamylphenol, prepared by direct alkylation of phenol, was free from *o*-(*α*-phenylallyl)-phenol.

Study of the rearrangement behavior of mixtures of allyl *β*-naphthyl ether with cinnamyl phenyl ether or 2-hexenyl phenyl ether showed that the rearrangement of allyl aryl ethers is intramolecular.

Resorcinol 2-hexenyl monoether and other hexenylresorcinols were prepared.

By use of a molecular still the polymeric products formed during pyrolysis of phenyl allyl ether were separated into a dimer and trimer of *o*-allylphenol. Considerable evidence supports *o*-(2-(*o*-allylphenoxy)-propyl)-phenol as the structure of the dimer.

EVANSTON, ILL. RECEIVED SEPTEMBER 21, 1936

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

A Series of N-Methyl Amides[1]

BY G. F. D'ALELIO[2] AND E. EMMET REID

In order to bring out the analogies of the N-monomethyl amides to the acids we have prepared the series from the normal acids, formic to stearic. Although some of these are recorded in the literature the data on all except the acetyl are fragmentary. We have compared a number of preparation methods which have been proposed for N-alkyl amides and have investigated some of their reactions. The physical properties of our compounds are given in Tables I and II and their melting points, along with those of the corresponding acids are plotted in Fig. 1. Using Swietoslawski's[3] values for the other elements the average value for the atomic refraction of nitro-

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF THE N-METHYL AMIDES

No.	B. p. °C.	Press., mm.	M. p. amide, °C.	M. p. acid, °C.	Diff.	Nitrogen, % Found	Nitrogen, % Calcd.
1	131.0	90	− 5.4	8.4	−13.8	23.64	23.72
2	140.5	90	28.0	16.6	11.4	19.05	19.17
3	146.0	90	−43.0	−20.8	−22.2	16.03	15.90
4	156.0	90	− 5.2	− 5.5	− 0.3	13.81	13.86
5	169.0	90	−25.5	−34.0	8.5	12.09	12.17
6	183.0	90	13.6	− 3.9	17.5	10.78	10.85
7	151.0	15	14.0	− 8.9	22.9	9.67	9.79
8	161.5	15	38.9	16.3	22.6	8.84	8.91
9	175.0	15	39.1	12.3	26.8	8.11	8.18
10	...	..	57.3	32.0	25.3	7.54	7.56
11	...	..	56.0	27.8	28.2	6.99	7.03
12	...	..	68.4	43.2	25.2	6.60	6.57
13	...	..	68.2	41.5	26.7	6.05	6.12
14	...	..	78.4	53.9	24.5	5.74	5.81
15	...	..	78.3	52.3	26.0	5.43	5.48
16	...	..	85.5	61.8	23.7	5.17	5.20
17	...	..	84.8	60.7	24.1	4.87	4.94
18	...	..	92.1	68.8	23.3	4.62	4.71

TABLE II

PHYSICAL PROPERTIES OF THE N-METHYL AMIDES OF THE LOWER ACIDS

No. of C atoms in acid	n^{2}_{D}	d^{0}_{4}	d^{25}_{4}	d^{35}_{4}	Mol. ref. Found	Mol. ref. Calcd.
1	1.4300	1.0114	0.9961	...	15.23	15.30
2	1.4301[a]	...	.9571	0.9481	20.51	19.91
3	1.4345	0.9508	.9304	...	24.64	24.51
4	1.4365	.9308	.9108	...	29.05	29.11
5	1.4401	.9239	.9033	...	33.61	33.72
6	1.4431	...	.8925	.8849	37.77	38.32
7	1.4450[b]	...	.8869	.8795	42.99	42.99

[a] The values for N-methyl acetamide were determined also over the following range of temperatures, n^{t}_{D} where t = 35, 1.4253; 33, 1.4263; 32, 1.4268; 31, 1.4272; 30, 1.4277; 29, 1.4282; 28, 1.4286; 27, 1.4290; 26, 1.4294.
[b] Franchimont and Klobbie, *Rec. trav. chim.*, **6**, 247 (1887), give sp. gr. 0.895 at 15° or 0.894^{15}_{4}. Their product had m. p. 9° and b. p. 265.6–266.5° at 758 mm.

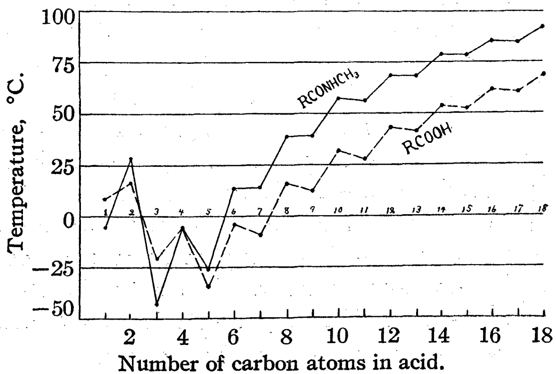

Fig. 1.—Melting points of acids and of their N-methyl amides.

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(1) From a part of the Ph.D. dissertation of G. F. D'Alelio, June, 1935.

(2) The Charles J. O'Malley Fellow of Boston College.

(3) Swietoslawski, THIS JOURNAL, **42**, 1945 (1920).

gen in these amides is 2.76. The curves for the melting points of these amides and of the acids are strikingly alike. The liquid N-methyl amides resemble the acids in viscosity. The lower members of the series are practically tasteless, but a peppery taste appears with the fourth and reaches a maximum value with the tenth, which has an intense burning taste and numbs the tongue. The toxicities increase likewise. Nos. 7, 8 and 9 are local anesthetics.[4]

Chemical Reactions

The mono-methyl amides, like acetamide,[5] form two types of hydrochlorides (a) $RCONHCH_3 \cdot HCl$ and (b) $(RCONHCH_3)_2 \cdot HCl$. In a non-polar solvent type (a) salts are formed, while in the absence of any solvent, type (b) result. Melting points and analyses of our preparations appear in Table III.

Table III

Melting Points and Analyses of the Hydrochlorides of the Methyl Amides

No.	Melting points, °C. $RCONHCH_3HCl$	$(RCONHCH_3)_2HCl$	Chlorine, % Calcd.	Found
1	82.8–85.0	......	37.13	37.00
2	67.2–69.4	......	32.42	32.50
3	....	84–85	19.43	19.38
4	....	106.4–108	16.83	16.79
5	....	17–20	14.85	14.79
6	....	—1 to 3	13.40	13.15
7	....	32–34	12.03	12.00
8	....	38–40	11.00	10.90

Sodium reacts readily with formamide[6] but hardly at all with its N-methyl derivative or with other N-methyl amides at room temperature. It does react with their solutions in boiling toluene. Amides form mercury derivatives[7] but the N-methylamides do not. Treatment of N-methyl acetamide with nitrous acid converts it into its nitroso compound, b. p. 116.3°, m. p. −8.5°, $n^{25}\text{D}$ 1.4415, d^{0}_{4} 1.1007, d^{25}_{4} 1.0709, mol. refr. 25.10, calcd. 25.32. Refluxing N-methyl acetamide with acetic anhydride gives N-methyldiacetamide,[3] b. p. 194.2°, m. p. −46.8°, $n^{25}\text{D}$ 1.4502, d^{0}_{4} 1.0904, d^{25}_{4} 1.0663, mol. refr. 28.9, calcd. 27.9. With phosphorus pentoxide a complicated reaction occurs: N-methyldiacetamide is formed in 19% yield. N-Bromo-N-methyl acetamide is obtained readily as light yellow prisms, m. p. 123.5° but is very unstable, readily giving up its bromine. It does not undergo the Hofmann[8] degradation which accords with the prediction of Stieglitz.[9]

Experimental

Preparation of N-Methyl Amides.—The most generally useful method was to drop the acid chloride very slowly, with constant stirring, into three moles of amine[10] in concentrated aqueous solution. For the first nine members the temperature was kept at −20 to −10° during the addition. The methyl amides were caused to separate by the addition of solid caustic potash to the mixture. The separated amide was dried over caustic potash, and distilled. For the higher members a large excess of amine was used, and cooling was effected by tap water. Troublesome emulsions result unless the acid chloride is added at an extremely slow rate. At the completion of the reaction the mixture was placed in a separatory funnel, the aqueous layer drawn off, and the amide taken up in benzene or ether. The solution was dried and the amide recovered by evaporation of the solvent and then recrystallized from anhydrous methanol. The yields run from 85 to 95%. Similar yields of the lower amides were obtained when the amine was passed into a solution of the acid chloride in dry toluene at −10° followed by the addition of 20% sodium hydroxide solution.

For comparison various other methods of preparing amides were tried. The reaction of dry methylamine on esters proved to be very slow but with an excess of the aqueous amine 68% of the heptamide was obtained after several days. From the sodium salt of an acid and methylamine hydrochloride as recommended by Verley[11] and Menschutkin[12] a good yield of the crude amide was obtained but it was difficult to purify. Acetamide[13] and its sodium salt[14] were methylated, yields 50–60%. The methyl amides of formic and acetic were obtained by passing the amine through the heated acids.[15]

N-Nitroso-N-methyl Acetamide.—To one mole of methyl acetamide and three moles of sodium nitrite dissolved in a minimum amount of water, concentrated hydrochloric acid was added slowly. When the reaction was complete the mixture was cooled, the oily layer separated, dried and distilled. On five runs the yields varied from 74–80%. *Anal.* % N calcd. 27.45; found 27.41.

N-Methyl Diacetamide.—N-Methyl acetamide was refluxed with 2.8 moles of acetic anhydride and the product fractionated in a precision still, yield 68%. *Anal.* % N calcd. 12.17; found 12.14.

N-Bromo-N-methyl Acetamide.—To 0.1 mole of N-methyl acetamide in 25 cc. of anhydrous ethyl acetate, 0.15 mole of bromine was added. Silver oxide was added slowly with rapid stirring until the bromine color disap-

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(4) Macht and D'Alelio, *Am. J. Physiol.*, **116**, 104 (1936).

(5) Titherly, *J. Chem. Soc.*, **79**, 411 (1901); Holden, *ibid.*, **101**, 1875 (1912); Pinner, *Ber.*, **25**, 1435 (1882).

(6) P. A. Magill, *Ind. Eng. Chem.*, **26**, 612 (1934).

(7) Strecker, *Ann.*, **103**, 324 (1858); Markownikoff, *Z. Chem.*, **6**, 533 (1863).

(8) A. W. Hofmann, *Ber.*, **18**, 2734 (1885); **19**, 1822 (1886); **35**, 3579 (1902).

(9) J. Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 48 (1903).

(10) Our thanks are due to E. I. du Pont de Nemours & Co., for a cylinder of methylamine.

(11) Verley, *Bull. soc. chim.*, [3] **9**, 691 (1893).

(12) Menschutkin, *Ber.*, **17**, 848 (1884).

(13) Nicholas and Erickson, This Journal, **48**, 2174 (1926).

(14) Walsh and Titherley, *J. Chem. Soc.*, **79**, 402 (1901).

(15) Mitchell and Reid, This Journal, **53**, 1879 (1931).

peared, the temperature being kept below 50°. The silver bromide was filtered off and the solution evaporated *in vacuo*. The resulting oil crystallized on standing in a vacuum desiccator. The crystals were washed free of bromine with carbon tetrachloride. *Anal.* % Br calcd. 52.58; found 52.60.

Thanks are due to Dr. John R. Ruhoff and Dr. Jane Dick Mayer for samples of the higher acids and esters.

Summary

N-Methyl amides of the acids from formic to stearic have been prepared and some of their physical and pharmacological properties determined. Some of them are local anesthetics and possess a peppery taste. Derivatives of some of them have been made.

BALTIMORE, MARYLAND RECEIVED NOVEMBER 14, 1936

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

Three Series of N-Substituted Aliphatic Amides[1]

BY G. F. D'ALELIO AND E. EMMET REID

In a previous article,[2] a series of N-methyl amides has been described. This investigation considers three series involving the same normal aliphatic acids, their hydroxyls being replaced by the groups (a) —$NHCH_2CH_2OH$, (b) —$N(CH_2CH_2OH)_2$ and (c) —$NHCH_2CH(OH)CH_3$. Some acyl derivatives of aminoethanol have been described[3,4] and since the completion of our work, a communication describing the first three ethanol amides has appeared.[5]

All of our compounds were prepared by heating the ethyl esters of the acids, already reported,[6,7] with the amine.[8] For the first six members of series (a), the ester was refluxed with a 25% excess of ethanolamine for six hours and the product fractionated. For the remainder of this series, 2 g. of the ester with a 3% excess of the amine was heated at 160° for six to ten hours. The higher ethanol amides were washed with dilute hydrochloric acid and recrystallized from 95% ethanol or from anhydrous methanol.

The diethanol amides gave the most trouble; the lower members melt too low for crystallization, boil too high for fractionation and are too soluble in organic solvents and water With the higher members the reaction products solidified to waxes. These were dissolved in the minimum amount of methanol, 5 volumes of water added and the mixture saturated with sodium chloride. The precipitated amides were filtered off and kept four months in a vacuum desiccator over sulfuric acid. They could then be crystallized from methanol–ether mixtures; average yield 70%.

The higher isopropanol amides were readily prepared from the amine and the ester. The solids were recrystallized from methanol, average yield 85%.

N-Ethanol benzamide was prepared by heating equivalent quantities of ethyl benzoate and ethanolamine in a flask in an oil-bath at 150° until the calculated amount of alcohol had distilled off. The solidified product was spread on a porous plate, desiccated over sulfuric acid and recrystallized from acetone, yield 95%, m. p. 67.6°, N calcd. 8.48; found 8.39%. This compound was made by Fränkel[3] who gave 67° as m. p. and by Wenker[5] who obtained it as an uncrystallizable liquid. The melting points are given in Tables I and II and plotted in Fig. 1.

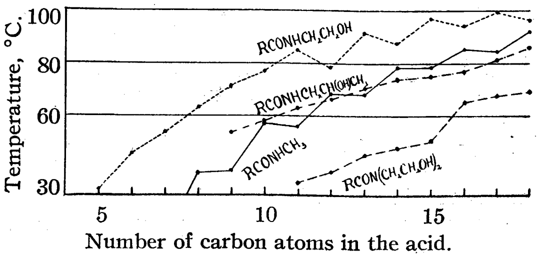

Fig. 1.—Melting points of the N-substituted amides.

The N-ethanol amides show slight alternation up to no. 11 where it suddenly becomes pronounced and then diminishes. This curve is the inverse of that of the N-methyl amides which is shown for comparison. The alternation is slight with the N-isopropanol amides and seems to

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[1] From a part of the Ph.D. dissertation of G. F. D'Alelio, Charles J. O'Malley Fellow of Boston College.

[2] G. F. D'Alelio and E. Emmet Reid, THIS JOURNAL, **59**, 109 (1937).

[3] Fränkel and Cornelius, *Ber.*, **51**, 1654–62 (1918).

[4] Knorr, *ibid.*, **36**, 1278 (1903).

[5] H. Wenker, THIS JOURNAL, **57**, 1079 (1935).

[6] Ruhoff and Reid, *ibid.*, **55**, 3827 (1933).

[7] Meyer and Reid, *ibid.*, **55**, 1583 (1933).

[8] Generously supplied by Carbide and Carbon Chemicals Corp.

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF N-ETHANOL AMIDES

No. C atoms in acid	M. p., °C.	n^{25}D	B. p., °C.	Mm.	Yield, %	% Nitrogen Calcd.	% Nitrogen Found
1	Glass	1.4785	150–155	2[a]	65	15.73	15.61
2	40	1.4710	155–160	2–3[a]	87	13.60	13.40
3	Glass	1.4681	160–168	1–2[a]	89	11.98	11.93
4	Glass	1.4672	155–162	1–1.5	78	10.69	10.60
5	32.0	1.4642	192	6	84	9.65	9.63
6	46.0				91	8.80	8.83
7	53.6				87	8.08	8.00
8	63.2				85	7.51	7.46
9	71.6				88	6.97	6.93
10	77.1				82	6.51	6.50
11	84.8				86	6.10	6.06
12	78.2				90	5.77	5.79
13	91.8				87	5.45	5.41
14	87.4				80	5.17	5.13
15	97.0				81	4.91	4.86
16	94.4				84	4.67	4.70
17	99.2				84	4.47	4.44
18	96.1				86	4.28	4.20

[a] Ref. (5) gives for no. 1, b. p. 191–193° (10 mm.), d^{25}_{25} 1.180; for no. 2 b. p. 195–196° (10 mm.), d^{25}_{25} 1.115; for no. 3 b. p. 201–203° (10 mm.), d^{25}_{25} 1.071. Ref 3 gives m. p. for no. 2 of 63–65° while we found 40° from a heating and cooling curve.

TABLE II

MELTING POINTS AND ANALYSES

No. C atoms in acid	Diethanol amides M. p., °C.	Diethanol amides Nitrogen, % Calcd.	Diethanol amides Nitrogen, % Found	Isopropanol amides M. p., °C.	Isopropanol amides Nitrogen, % Calcd.	Isopropanol amides Nitrogen, % Found
9	Glass	..	..	53.8	6.52	6.50
10	Glass	..	..	58.1	6.10	6.00
11	34.9	5.13	5.08	63.1	5.76	5.70
12	38.7	4.88	4.81	66.6	5.45	5.43
13	45.3	4.66	4.64	71.0	5.17	5.15
14	47.9	4.44	4.40	74.2	4.91	4.87
15	50.9	4.25	4.20	75.1	4.75	4.69
16	65.1	4.08	4.00	78.2	4.53	4.54
17	67.9	3.93	3.88	82.0	4.34	4.30
18	69.7	3.79	3.75	86.1	4.15	4.13

invert at no. 14. The melting points of the N-diethanol amides appear to rise in groups of three. Pharmacological results have been published.[9] For the ninth members of the four series of N-substituted amides the activities are in the order: $RCONHCH_3 > RCONHCH_2CH_2OH > RCON(CH_2CH_2OH)_2 > RCONHCH_2CH(OH)CH_3$.

Summary

The N-ethanol amides of the normal acids from formic to stearic have been prepared and characterized. The corresponding N-diethanol and N-isopropanol amides have been made of the higher acids. Comparative pharmacological effects are also reported.

BALTIMORE, MARYLAND RECEIVED NOVEMBER 14, 1936

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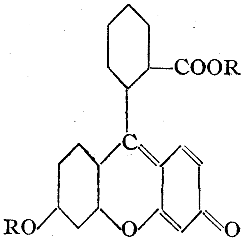
[9] Macht and D'Alelio, *Am. J. Pharmacol.*, **116**, 104 (1936).

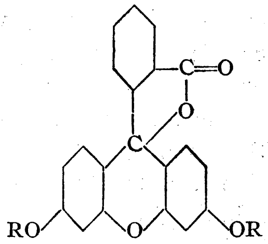
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Alkenyl Derivatives of Fluorescein

BY CHARLES D. HURD AND LOUIS SCHMERLING[1]



(A)



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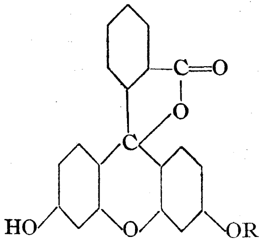
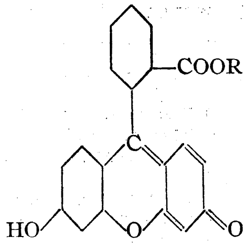


(C)



(D)

R represents $CH_2{=}CHCH_2{-}$, $C_2H_5CH{=}CHCH_2{-}$, $n\text{-}C_3H_7CH{=}CHCH_2{-}$.

Surprisingly few O-alkylated derivatives of fluorescein have been prepared. Only the methyl and ethyl derivatives are reported in the literature, but they have been investigated by many workers[2] chiefly because of the confusion arising from difficulties involved in their purification. In the present study, the allyl, pentenyl and hexenyl derivatives were synthesized. The various types involved are the "ether ester" (A), the "diether" (B), the "monoether" (C) and the "monoester" (D).

Two general methods of synthesis were used. In the first, fluorescein was reacted with the

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[1] Parke, Davis and Company Fellow, 1933–1935.

[2] Fischer and Hepp, *Ber.*, **27**, 2790 (1894); **28**, 396 (1895); **46**, 1951 (1913); Nietzki and Schroeter, *ibid.*, **28**, 44 (1895); Herzig and Meyer, *ibid.*, **28**, 3258 (1895); Kehrmann and Dingler, *ibid.*, **42**, 810 (1909); **46**, 3028 (1913); **47**, 84 (1914); von Liebig, *J. prakt. Chem.*, **85**, 97, 241 (1912); **86**, 472 (1912); **88**, 26 (1913); *Ber.*, **46** 3593 (1913).

TABLE I

O-ALKENYL DERIVATIVES OF FLUORESCEIN

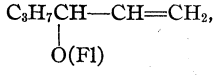
Symbol	Descriptive name of compound	Systematic name
I	Allyl ether ester	Allyl 6-alloxy-9-phenylfluorone-11-carboxylate
II	Allyl diether	3,6-Dialloxyfluoran
III	Allyl ether	3-Alloxy-6-hydroxyfluoran
IV	Acetate of III	3-Alloxy-6-acetoxyfluoran
V	Allyl ester	Allyl resorcinolbenzein-11-carboxylate
VI	Pentenyl ether ester	γ-Ethylallyl 6-(γ-ethylalloxy)-9-phenylfluorone-11-carboxylate
VII	Pentenyl diether	3,6-Di-(γ-ethylalloxy)-fluoran
VIII	Pentenyl ether	3-γ-Ethylalloxy-6-hydroxyfluoran
IX	Acetate of VIII	3-γ-Ethylalloxy-6-acetoxyfluoran
X	Hexenyl ether ester	γ-*n*-Propylallyl 6-(γ-*n*-propylalloxy)-9-phenylfluorone-11-carboxylate
XI	Hexenyl diether	3,6-Di-(γ-*n*-propylalloxy)-fluoran
XII	Hexenyl ether	3-γ-*n*-Propylalloxy-6-hydroxyfluoran
XIII	Acetate of XII	3-γ-*n*-Propylalloxy-6-acetoxyfluoran

alkenyl bromide in acetone solution in the presence of potassium carbonate. All four type compounds were obtained in the reaction mixture. The first step in separating them was based on the fact that A and B are alkali-insoluble, whereas C, D and unreacted fluorescein are alkali-soluble. Separation of orange colored A from colorless B was accomplished by virtue of the fact that the latter is more soluble in carbon tetrachloride and less soluble in ethyl alcohol. The monoether and the monoester were separated from the fluorescein by precipitation from the alkaline solution with carbon dioxide. The amount of material so obtained was usually very small. The dark-red monoallyl ester was found to be less soluble in cold alcohol than the nearly colorless monoether and was separated from it by use of this property.

The second method, which has the advantage of being much more rapid than the first, was applied to phenols as well as to fluorescein types. It involves the reaction of the alkenyl bromide with the sodium phenolate in an aqueous acetone solution. The proportions of water and acetone were so adjusted as to give a clear solution. With this procedure, there were higher yields of C, lower yields of B, and approximately the same yields of A, as in the first method. Since little unreacted fluorescein remained, the monoether (C) could be obtained in a pure state by acidifying the alkaline solution and recrystallizing the precipitate from ethyl alcohol. It was not found possible to isolate any of the monoester by this second method.

It was found as expected that the various allyl and alkenyl ethers (types A, B and C) rearranged on heating to form C-substituted fluoresceins. When, for example, the allyl diether was heated to 210°, an exothermic reaction occurred, and most of the material became alkali-soluble. The product consisted chiefly of 2,7-diallylfluorescein with some 2-allylfluorescein and fluorescein. The presence of the latter compounds is analogous to the formation of phenol[3] from phenyl allyl ether. In the present study, fluorescein and the C-alkylated rearrangement products were found to be too similar in physical and chemical properties to permit the complete separation of the latter from the former.

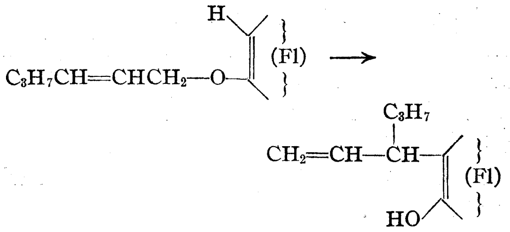
The structure of the hexenyl portion of fluorescein hexenyl diether was determined by ozonolysis. It was found that the volatile acid obtained from the ozonide was a mixture of formic and butyric acids, with butyric considerably in excess. The butyric acid would come from $C_3H_7CH{=}CHCH_2{-}O{-}(Fl)$ and the formic from



$$\underset{\displaystyle O(Fl)}{C_3H_7CH}{-}CH{=}CH_2,$$

wherein (Fl) represents the fluorescein residue. Such a result indicates that the hexenyl bromide used in the synthesis of the ether was an equilibrium mixture of 1-bromo-2-hexene and 3-bromo-1-hexene.

Ozonolysis of the rearrangement product of the diether gave evidence which supported the idea



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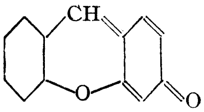
(3) Hurd and McNamee, THIS JOURNAL, **54**, 1648 (1932).

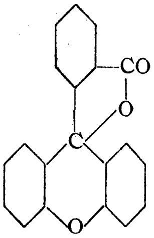
that the "wandering" group undergoes inversion of an allylic type. Formic and butyric acids were indicated as before, but this time it was the formic which was in excess.

The saponification of the diallyl ether ester led to some very interesting results. It was found that the solvent used during the reaction was a determining factor. Thus, it was shown that either fluorescein, or its monomethyl, ethyl or allyl ethers could be obtained by using, respectively, water, methanol, ethanol or allyl alcohol (or aqueous acetone) as the solvent. A similar observation was made by von Liebig[4] who obtained the monoethyl ether of fluorescein in an attempt to prepare the monomethyl ether by saponifying the dimethyl ether ester with ethyl alcoholic potash.

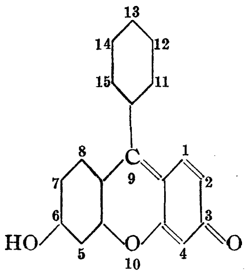
The O-alkenyl compounds studied are listed in Table I. The systematic names are derived from the following nuclei: fluorone (E), fluoran (F) and resorcinolbenzein (G).



(E)



(F)



(G)

The allyl ether ester (I) and pentenyl ether ester (VI) were tested bactericidally in the Parke, Davis and Company Laboratories, but were found to be ineffective (phenol coefficients less than 50 toward *Staph. aureus*). Their extreme insolubility may have been a contributing factor.

Two new reactions of fluorescein are also recorded. One is the production of diacetylfluorescein by addition of ketene, and the other is the formation of 3,6-dichlorofluoran by reaction with thionyl chloride.

Experimental Part

Diacetylfluorescein.—Ketene, generated at the rate of 0.1 mole per hour, by passing acetone vapors over a hot platinum filament,[5] was passed through a suspension of 1.66 g. of red fluorescein in 50 cc. of acetone. The calculated time to obtain the diacetate was six minutes. In five minutes, it was noticed that the fluorescein was beginning to dissolve. In seven minutes, solution was complete and the flow of ketene was stopped. The acetone was evaporated. The residual oil solidified on the addition of ethanol The first crystallization from 100 cc. of hot alcohol gave crystals which melted at 204° (the same as that observed with material prepared from fluorescein and acetic anhydride). A second recrystallization raised the m. p.[6] to 205°; yield, 1.9 g., or 91%.

3,6-Dichlorofluoran.—Ten cc. (16.5 g.) of thionyl chloride was added to 5 g. of red fluorescein. A yellow color was imparted to the mass. It turned red and dissolved after an hour of refluxing. The heating was continued for another hour and the excess of thionyl chloride was distilled off. The red-brown residue was digested with water, then treated with dilute sodium hydroxide, and finally crystallized from hot toluene. White crystals of 3,6-dichlorofluoran, m. p. 262°, uncorr., were obtained; yield 5.4 g., or 90%. The m. p. was unchanged by recrystallization from acetic anhydride or from alcohol. When dissolved in hot toluene and precipitated therefrom by one to two volumes of alcohol, the m. p. changed to 256°.

3,6-Dichlorofluoran, prepared from fluorescein and phosphorus pentachloride according to Baeyer's direction,[7] melted at 255°. Baeyer reported 252°. When reduced with zinc dust and alcohol,[8] both products yielded fluorescein dichloride, m. p. 229°.

Preparation of Ethers

Allyl *p*-Cresyl Ether.—This ether was prepared by a new method. An aqueous solution of sodium *p*-cresolate was prepared from 5.4 g. of *p*-cresol, 2.0 g. of sodium hydroxide and 30 cc. of water. To this were added 6.1 g. of allyl bromide and sufficient acetone (30 cc.) to give a single clear solution. The solution was allowed to stand at room temperature for four hours during which there separated an oily supernatant layer. The oil was extracted with petroleum ether, washed with water, dried over potassium carbonate, and distilled. Allyl *p*-cresyl ether was obtained as a colorless oil boiling at 96–98° (15 mm.); n^{24}_D 1.5157. These constants agree with those in the literature.[9] The yield was 5.3 g., which is 72%.

Hexenyl *p*-Cresyl Ether.—A solution was made of 4.4 g. of *p*-cresol and 1.6 g. of sodium hydroxide in 50 cc. of water. Then 6.5 g. of 1-bromo-2-hexene in 100 cc. of acetone was added. In four hours the mixture had separated in two layers which were separated by extraction with petroleum ether. After washing, drying and

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[4] Von Liebig, *J. prakt. Chem.*, **88**, 26 (1912).

[5] Hurd and Williams, THIS JOURNAL, **58**, 965 (1936).

[6] The m. p. is reported variously in the literature. Orndorff and Hemmer, THIS JOURNAL, **49**, 1275 (1927), listed 200°; von Liebig, *J. prakt. Chem.*, **85**, 241 (1912) reported 205–206°; Sah and Yen, *Chem. Zentr.*, **104**, I, 3560 (1933), found 206–207°.

[7] Baeyer, *Ann.*, **183**, 18 (1876).

[8] Meyer, *Ber.*, **25**, 1387 (1892).

[9] Claisen and Eisleb, *Ann.*, **401**, 44 (1913).

distilling, the colorless ether was obtained in 66% yield (5 g.); b. p. 142–146° (14 mm.), n^{26}_D 1.5071.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.46. Found: C, 81.7; H, 9.39.

Preparation of O-Alkenyl Derivatives of Fluorescein

The properties and analyses of the various compounds are summarized in Table II.

TABLE II

PROPERTIES OF COMPOUNDS

Symbol	Color	M. p., °C.	Analyses,[a] % Calcd. C	H	Found C	H
I	Orange	155	75.69	4.89	75.16	5.02
II	Pale yellow	124	75.69	4.89	75.37	4.61
III	Pale yellow	205	74.17	4.32	73.97	4.61
IV	Colorless	143	72.46	4.35	72.01	4.43
V	Dark red	233	74.17	4.32	73.76	4.53
VI	Orange	118	76.91	6.00	76.97	5.89
VII	Pale yellow	131	76.91	6.00	76.89	5.95
VIII	Yellow	220	75.00	5.00	74.66	5.22
IX	Yellow-white	108	73.30	4.97	73.12	4.85
X	Orange	109	77.42	6.45	76.69	6.24
XI	Pale cream	103	77.42	6.45	77.30	6.50
XII	Pale yellow	187	75.36	5.31	74.95	5.37
XIII	Yellow-white	154	73.68	5.26	73.68	5.35

[a] All analyses except XI were performed by Mr. M. A. Pollack.

The Allyl Ether Ester of Fluorescein (I)

First Method.—Thirty-three grams (0.1 mole) of fluorescein was mixed with 28 g. (0.2 mole) of potassium carbonate. A solution of 24 g. (0.2 mole) of allyl bromide in 300 cc. of acetone was added. After refluxing with stirring for twelve hours, the mixture was poured into 500 cc. of cold water. The allyl ether ester and the allyl diether of fluorescein precipitated, while the unreacted fluorescein as well as a small amount of the monoallyl ether and the monallyl ester dissolved, giving rise to a deep red solution which exhibited a green fluorescence. The orange precipitate was filtered off, washed with water, and dried in a desiccator. On recrystallizing the 30 g. of crude material from 350 cc. of carbon tetrachloride, there was obtained 16 g. of the orange-colored ether ester, m. p. 155°. Concentration of the mother liquor to 75 cc. yielded an additional 1.2 g. of the compound, bringing the total yield to 17.2 g. or 42%. On complete evaporation of the solvent, there was left a brown gummy residue from which the allyl diether could be obtained.

Second Method.—Thirty-eight grams (0.1 mole) of the disodium salt of fluorescein was dissolved in 250 cc. of water and a solution of 24 g. (0.2 mole) of allyl bromide in 150 cc. of acetone was added, giving a single clear solution. (The sodium salt was prepared by adding an excess of fluorescein to a solution of sodium hydroxide, filtering, and evaporating the filtrate to dryness.) The aqueous acetone solution was refluxed for two hours during which time the allyl ether ester and the monoallyl ether separated as a dark red oil. On pouring the supernatant solution into water, an orange, colloidal solution was obtained. Dilute alkali was added to dissolve the monoallyl ether and cause the precipitation of the ether ester as a flocculent orange precipitate. The dark red oil was dissolved in 50 cc. of acetone, poured into water, and the resulting colloidal solution treated similarly with alkali. After filtering and washing the precipitates, the combined yield of crude alkali-insoluble material was 25 g. On recrystallizing from carbon tetrachloride there was obtained 18 g. of (I), m. p. 155°. This is 43.5% of the theoretical.

The second method is not only more rapid than the first, but it is also to be preferred since a 30% yield of the monoallyl ether rather than unreacted fluorescein was obtained from the alkaline filtrate. It was found that the yield of ether ester could be made practically quantitative by using a 25% excess of allyl bromide and by adding sufficient acetone during the refluxing to maintain a clear solution.

The Allyl Diether of Fluorescein (II).—The brown, gummy residue from the final mother liquor from the recrystallization of (I), prepared by the first method, was dissolved in 30 cc. of hot 95% ethanol. Dark brown crystals began to separate on cooling. These were filtered and washed with alcohol to remove most of the brown impurity. On recrystallizing from 20 cc. of hot alcohol there was obtained 3.6 g. of pale yellow crystals which melted sharply at 124°.

The Allyl Ether of Fluorescein (III).—The alkaline filtrates from the synthesis of (I) by the second method were combined and acidified with hydrochloric acid. There was obtained a yellow precipitate which coagulated to form a tan gum on warming. (This serves to distinguish the monoether from unreacted fluorescein, the yellow form of which coagulates as red granules on warming in hydrochloric acid solution.) The coagulated precipitate was washed by decantation and then dissolved in 75 cc. of hot alcohol. On standing overnight 9.2 g. of the pale yellow allyl ether of fluorescein, m. p. 205°, separated. An additional 2.1 g. of the compound was obtained by evaporating the mother liquor and treating the resulting tar with a solution of 0.5 cc. of acetone in 10 cc. of alcohol which removed the impurities, leaving the ether undissolved. The total yield of (III) was 30% of the theoretical.

Acetate of (III).—This derivative was prepared by dissolving 0.5 g. of (III) in 2 cc. of acetic anhydride and heating for five minutes. After several recrystallizations from ethanol, the acetate was obtained colorless, m. p. 143°.

The Allyl Ester of Fluorescein (V).—The alkaline filtrate from the synthesis of (I) by the first method was acidified with hydrochloric acid and the yellow precipitate filtered and washed. This gave 10.8 g. of material which was dissolved in a solution of 4 g. of sodium carbonate in 200 cc. of water. Carbon dioxide was bubbled through the solution for several hours, at the end of which time 2.4 g. of orange-red solid had separated. This was a mixture of the allyl ether and the allyl ester. The former was extracted by washing the mixture with several 10-cc. portions of warm ethanol. The residue was dissolved in 4 cc. of hot ethanol. The solution was intensely fluorescent. On cooling, (V) slowly crystallized in small clusters of dark red crystals, m. p. 233°.

The pentenyl ether ester (VI) and the pentenyl diether of fluorescein (VII) were obtained in essentially the same

TABLE III

Substance heated	Compound formed Symbol	Compound formed Name	M.p., °C.	Analyses Calcd. C	Analyses Calcd. H	Analyses Found C	Analyses Found H
III	XIV	2-Allylfluorescein	168–176	74.17	4.32	73.57	4.46
II	XV	2,7-Diallylfluorescein	158–161	75.69	4.89	74.99	4.78
I	XVI	Allyl 2-allylresorcinolbenzein-11-carboxylate (Allyl ester of 2-allylfluorescein)	137–143	75.69	4.89	74.40	4.84
VIII	XVII	2-Pentenylfluorescein	156–160	75.00	5.00	74.25	4.86
XI	XVIII	2,7-Dihexenylfluorescein	135–140	77.42	6.45	75.28	6.52

way as the corresponding allyl derivatives, (I) and (II), using the first method. The mixture of 1-bromo-2-pentene[10] (0.1 mole), fluorescein (0.05 mole) and potassium carbonate (0.1 mole) in acetone (50 cc.) was refluxed for twelve hours over a period of two days. On pouring into water, an oily layer separated. The oil solidified after four hours in the ice box. It was filtered, washed with a 1% solution of sodium hydroxide, then water and finally dried. In this case, it was found that a better separation of the two isomers could be obtained by dissolving the ether ester in cold ethanol, which procedure left the diether undissolved. Recrystallized from hot ethanol, the pentenyl diether of fluorescein was obtained as pale yellow needles, m. p. 131°.

The pentenyl ether ester was obtained as orange-colored flakes, m. p. 118°, by precipitation from the alcoholic solution with water and recrystallization from carbon tetrachloride. The yields of diether and ether ester, respectively, were 23 and 17%.

The pentenyl ether of fluorescein (VIII) was obtained in 32% yield by the same method as that used to prepare the allyl ether (III). Its melting point, 220°, was found to depend somewhat on the rate of heating, for rearrangement takes place on melting. **Its acetyl derivative (IX)**, prepared analogously to IV, melted at 108°. The crystallization from alcohol required several hours.

The hexenyl ether ester (X) and the hexenyl diether of fluorescein (XI) were prepared in the same manner as the pentenyl compounds. It was necessary to reflux with stirring the mixture of 1-bromo-2-hexene[11] (0.2 mole) fluorescein (0.1 mole), and potassium carbonate (0.2 mole) in acetone (120 cc.) for sixty hours over a period of eight days. The first sign of reaction (*i. e.*, the formation of alkali-insoluble material) was not observed until the fifth day, after thirty-six hours of refluxing. The yields of diether and of ether ester, respectively, were 22 and 12%.

The Hexenyl Ether of Fluorescein (XII).—This compound and its acetyl derivative (XIII) were obtained by the same methods as for the allyl and pentenyl compounds. Like the other monoethers, the impure yellow crystals of the monohexenyl ether tended to turn orange when exposed to air and alcohol. It was only after three crystallizations from ethanol that it was obtained as pale yellow crystals, m. p. 187°; yield 12%.

Pyrolysis of the Ethers

General Procedure.—The compound (2–5 g.) was heated in a test-tube immersed in an oil-bath. Inner and outer temperatures were recorded. In all cases an exothermic reaction occurred at 210–220°, at which time the melt became viscous and darkened in color. The temperature was maintained at 210–220° for about one hour. The material was cooled, and the friable, dark red glass so obtained was crushed and extracted with a hot 5% solution of sodium bicarbonate. (In the case of the product from (I) it was necessary to use a 0.5% solution of sodium hydroxide.) The alkaline solutions were strongly fluorescent. The filtered alkaline solution was acidified, thereby precipitating the substituted fluorescein as a yellow-orange precipitate (yields, 50%) which formed a dark red glass on drying in an oven at 115°. The compounds were readily soluble in alcohol, acetone, ethyl acetate, glacial acetic acid or dioxane but insoluble in petroleum ether. In no case was it found possible to recrystallize the product from an organic solvent or combination of solvents.

The compounds treated in this manner were the allyl ether (III), the allyl ether ester (I), the allyl diether (II), the pentenyl ether (VIII), and the hexenyl diether (XI). Data regarding the substances formed are collected in Table III. Since purification was only by bicarbonate extraction and subsequent acidification, high purity for the compounds could not be expected. Analyses were fairly satisfactory in most cases, however. Small amounts of fluorescein or other by-products of the pyrolysis were undoubtedly present.

The material insoluble in sodium bicarbonate was washed with 10% sodium hydroxide, dissolved in alcohol and precipitated therefrom by water. About 0.3–0.6 g. of orange-yellow solid was obtained in each case. These were probably the cumarane analogs of XIV–XVIII.

Ozonolysis of Fluorescein Hexenyl Diether.—One gram (0.002 mole) of XI in 60 cc. of dry carbon tetrachloride was ozonized, the ozonide hydrolyzed with warm water and the aldehydes liberated were oxidized to acids by warming for four hours with a mixture of sodium hydroxide (1 g.) and silver oxide (from 3 g. of silver nitrate). After filtration, acidification with dilute sulfuric acid and refiltration, the filtrate was distilled to obtain the volatile acids. Both formic and butyric acids were identified, the former by permanganate titration and the latter (via the sodium salt and *p*-bromophenacyl bromide) as *p*-bromophenacyl butyrate, m. p. 61–63°. On the assumption that these were the only two volatile acids, they were analyzed by the Duclaux method and found to be in the ratio of 30:70 (formic:butyric). This assumption may not be wholly justified but the answer is valuable at least qualitatively.

Ozonolysis of 2,7-Dihexenylfluorescein.—Ozonolysis of XVIII (0.5 g.) and subsequent treatment as before yielded a mixture of volatile acids which was high in formic acid as revealed by permanganate titration.

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[10] Hurd and McNamee, THIS JOURNAL, **59**, 104 (1937).

[11] Hurd and Parrish, *ibid.*, **57**, 1732 (1935).

Duclaux analysis seemed to show 85% formic and 15% butyric acids, but here again the possible presence of other volatile acids limits the reliability of this quantitative figure. It does serve to demonstrate the preponderance of formic acid in the mixture, however.

Hydrolysis and Alcoholysis of (I)

In Water.—Three grams of the allyl ether ester was refluxed with a solution of 2 g. of potassium hydroxide in 100 cc. of water. The compound slowly dissolved, giving an intensely fluorescent solution. Saponification was complete after thirty minutes. Acetic acid was added to the clear solution until incipient precipitation. Filtration yielded 0.35 g. of the allyl ether (III); m. p. 204° after crystallization from ethyl alcohol. Complete acidification of the filtrate yielded 1.4 g. of material which was shown to be fluorescein; m. p. of the diacetate, 203–204°.

In Allyl Alcohol.—Two grams of the allyl ether ester was dissolved in 20 cc. of dry allyl alcohol. One gram of crushed sodium hydroxide was added, and the mixture was refluxed for one hour. The completeness of the reaction was determined by pouring a test portion into water; a clear solution indicated that the saponification was complete. Part of the alcohol was then distilled off and the residue poured into 100 cc. of water, filtered to remove traces of insoluble impurities, and acidified with hydrochloric acid. There was obtained 1.8 g. of (III), m. p. 205° (recrystallized from ethyl alcohol); a mixed m. p. with an authentic sample showed no depression.

In Aqueous Acetone.—One gram of the allyl ether ester was dissolved in 50 cc. of acetone and 1.5 g. of sodium hydroxide dissolved in 10 cc. of water was added. Two layers were formed. Refluxing for two hours resulted in very little reaction. When, however, sufficient water to give a single, clear solution was added, the solution almost immediately showed a green fluorescence and after ten minutes saponification was complete. The solution was poured into 100 cc. of water and acidified. The tan precipitate thus obtained melted at 197–200°. One recrystallization from alcohol yielded 0.5 g. of the pure allyl ether, m. p. 205°.

This procedure was found to be quite satisfactory for obtaining the allyl monoether (III), using the crude ether ester prepared by the second method described above. The yield of (III) was 55–65%, with fluorescein formed as a by-product.

In Methanol.—The procedure and quantity of materials were the same as in the case of allyl alcohol. The product formed on acidifying the alkaline solution melted at 262–265°; yield 1.3 g. On recrystallization from 95% ethyl alcohol, very pale yellow crystals, m. p. 266°, were obtained. The melting point given in the literature for fluorescein methyl monoether[12] is 262, 265 or 266°. The identity of the monoether was confirmed by converting it to the dimethyl ether ester by refluxing 0.8 g. of the compound and 2 cc. of concentrated sulfuric acid in 20 cc. of methanol for eight hours. The solution was poured into dilute alkali and the orange precipitate filtered off. Recrystallized from ethyl acetate, it melted at 208°; yield 0.6 g.

3-Methoxy-6-acetoxyfluoran (Acetate of Fluorescein Methyl Ether).—This new ester was obtained by heating 0.5 g. of fluorescein methyl monoether in 2 cc. of acetic anhydride and working up the product in the usual manner: m. p. 141° (recrystallized from ethyl alcohol).

Anal. (By Mr. M. A. Pollack) Calcd. for $C_{23}H_{16}O_6$: C, 71.13; H, 4.12. Found: C, 70.95; H, 4.10.

In Ethanol.—The method and results were similar to those in the experiments with the other two alcohols. Acidification of the alkaline solution yielded 1.35 g. of tan material. It was purified from 95% ethyl alcohol from which it crystallized in nearly colorlesss crystals, m. p. 250°. This is correct for fluorescein ethyl monoether.[13] Its identity was confirmed by preparing the monoacetyl derivative, m. p. 222°.

Summary

β,γ-Unsaturated ethers of fluorescein have been synthesized. These include the allyl, pentenyl and hexenyl monoethers, diethers and ether esters. The monoallyl ester also has been prepared.

The behavior of these ethers toward heat is analogous to that of the other allyl aryl ethers. Rearrangement gives rise to C-alkenylated fluoresceins with attachment to the nucleus taking place at the gamma-carbon atom of the allyl chain.

The hydrolysis or alcoholysis of the diallyl ether ester of fluorescein has been shown to yield fluorescein, the monomethyl ether, the monoethyl ether, or the monoallyl ether when water, methanol, ethanol or allyl alcohol (or aqueous acetone), respectively, are used as solvent. The acetate of fluorescein methyl ether was prepared.

It was shown that diacetylfluorescein may be made very readily from fluorescein and ketene. 3,6-Dichlorofluoran was suitably prepared from fluorescein and thionyl chloride.

A rapid, new method of synthesis of alkenyl aryl ethers was presented.

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[12] Von Liebig, *J. prakt. Chem.*, **88**, 39 (1913).

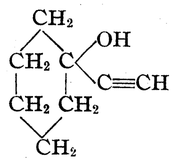
[13] Nietzki and Schroeter, *Ber.*, **28**, 56 (1895).

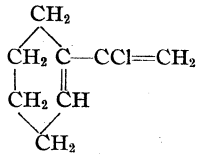
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

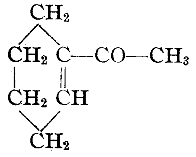
The Rearrangement of Ethynylcarbinols

BY CHARLES D. HURD AND ROBERT E. CHRIST

Recently, it was established[1] that 1-ethynyl-1-cyclohexanol (I) was converted by thionyl chloride and pyridine into 1-α-chlorovinyl-1-cyclohexene (II). Some years earlier, Rupe[2] had announced the transformation of (I) by formic acid into cyclohexylideneacetaldehyde, $(CH_2)_5$-C=CHCHO, not 1-acetyl-1-cyclohexene (III). In its enolized form (III) would be analogous to (II). The improbability that two acidic reagents should influence the ethynylcarbinol by essentially different mechanisms caused us to inspect Rupe's evidence. Curiously, it all supported the ketone (III), yet the aldehyde structure was assigned on the basis of delicate color reactions (Schiff's reagent and Angeli's reagent).


(I)

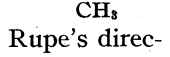

(II)


(III)

Evidence against the aldehyde formula was the non-formation of cyclohexylideneacetic acid with silver oxide. Ozonization supported (III) inasmuch as adipic acid was the reaction product instead of cyclohexanone. Excellent evidence for (III) was its behavior on catalytic hydrogenation. The material obtained boiled at 69° (12 mm.) and gave a semicarbazone of m. p. 171–172°. These are the constants for cyclohexyl methyl ketone[3] and its semicarbazone, rather than for cyclohexylacetaldehyde[4] (b. p. 79–80° (10 mm.); semicarbazone, m. p. 132–134°). Fischer and Löwenberg[5] had occasion to doubt the conclusion of Rupe and, in repeating the work, found that the hydrogenated product was actually cyclohexyl methyl ketone.

Rupe has also studied the rearrangement of about a dozen other ethynylcarbinols. In a few cases, namely, 1-ethynyl-3-(and 4-)-methyl-1-cyclohexanol and 1-ethynyl-2-methyl-5-isopropyl-1-cyclohexanol, rearrangement was reported[6] to yield unsaturated ketones of type III. The majority of the reactions, however, have been stated to yield the unsaturated aldehydes. No suggestion was included to explain why ketones were formed in a few cases and aldehydes in others. The aldehyde-forming carbinols included[7] ethynylmethylalkylcarbinol (alkyl = isohexyl, *t*-butyl, phenyl, isobutyl, β-phenylethyl), 1-ethynyl-2-(or 5)-isopropyl-5-(or 2)-methyl-1-cyclohexanol, and ethynylfenchyl alcohol. In these cases, as with 1-ethynyl-1-cyclohexanol, the interpretation of the evidence seemed questionable. Hence this matter was investigated and ethynylmethylphenylcarbinol, 1-ethynyl-1-cyclohexanol, and ethynylbornyl alcohol, a new compound, were selected for study. In none of these cases was any evidence found for the aldehyde structures postulated by Rupe. The evidence for ketones as rearrangement products was very convincing.

That (III) was the rearrangement product of (I) was confirmed by synthesizing 1-acetyl-1-cyclohexene from cyclohexene,[8] acetyl chloride, and aluminum chloride, preparing its semicarbazone (m. p. 220–221°), and proving its identity to the semicarbazone of (III), from (I), by a mixed melting point determination.

Ethynylmethylphenylcarbinol,

$C_6H_5\underset{CH_3}{C}(OH)$—C≡CH, was prepared according to Rupe's directions, but the oil (b. p. 122–130° (12 mm.); semicarbazone, m. p. 201°) which was obtained in small yield during reaction with formic acid was not β-phenylcrotonaldehyde (IV) as stated by Rupe and Giesler[9] but was simply acetophenone.

$$C_6H_5C(CH_3){=}CHCHO \quad (IV)$$
$$CH_2{=}C(C_6H_5)COCH_3 \quad (V)$$

The bulk of the reaction product was a tar which

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[1] Hurd and Jones, THIS JOURNAL, **56**, 1924 (1934).

[2] Rupe, Messner and Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

[3] Bouveault, *Bull. soc. chim.*, [3] **29**, 1051 (1903); Wallach, *Ann.*, **360**, 47 (1908); **389**, 192 (1912).

[4] Wallach, *Ann.*, **359**, 313 (1908); Skita, *Ber.*, **48**, 1694 (1915).

[5] Fischer and Löwenberg, *Ann.*, **475**, 203 (1929).

[6] Rupe and co-workers, *Helv. Chim. Acta*, **14**, 701 (1931); **16**, 685 (1933).

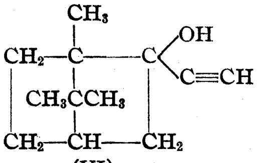
[7] Rupe and co-workers, *ibid.*, **11**, 656, 965 (1928); **12**, 193 (1929); **14**, 687, 708 (1931); **17**, 283 (1934); **18**, 542 (1935).

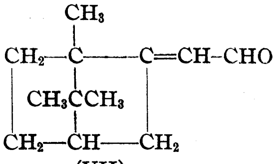
[8] Darzens, *Compt. rend.*, **150**, 707 (1910); Wallach, *Ann.*, **360**, 46 (1908).

[9] Rupe and Giesler, *Helv. Chim. Acta*, **11**, 656 (1928).

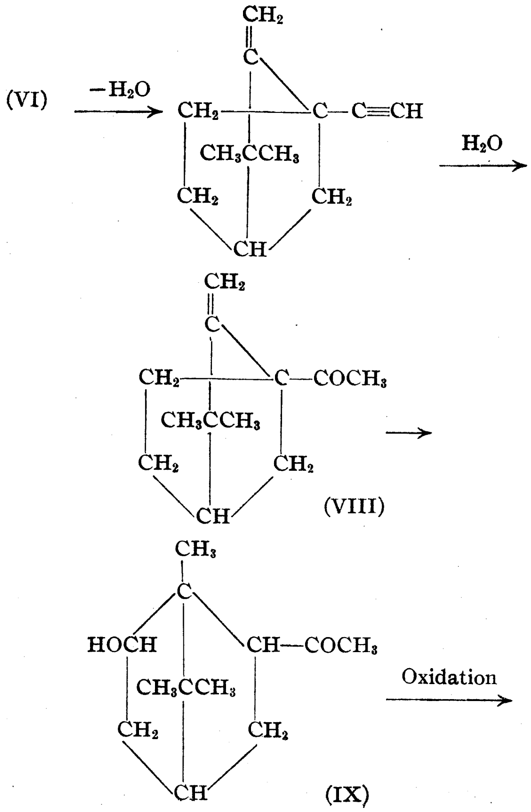
probably came *via* phenylbutenone (V). Both IV and V possess conjugated systems but V, with its unsubstituted methylene carbon, represents a type which is particularly susceptible to polymerization.

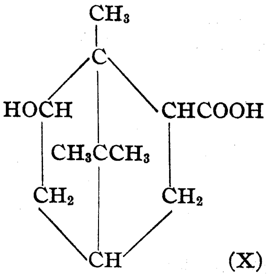
Ethynylbornyl alcohol (VI) was synthesized from camphor, acetylene and metallic sodium. A smooth rearrangement occurred with formic acid. The product, however, was not the aldehyde (VII) but was the ketone (IX).


(VI)

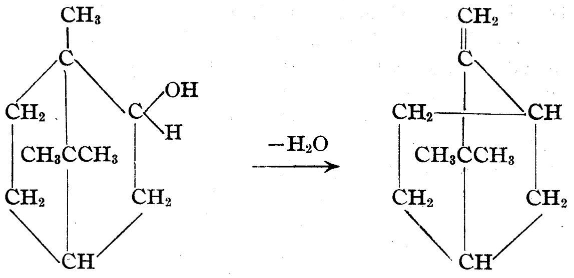

(VII)

In the first place, no acid was obtainable by the prolonged action of silver oxide. Secondly, analysis corresponded to $C_{12}H_{20}O_2$ rather than $C_{12}H_{18}O$. Finally, oxidation by ozone yielded 6-hydroxy-2-camphanecarboxylic acid (X). From these data, it is apparent that the product of rearrangement is 2-acetyl-6-hydroxycamphane (IX). Since the latter is a γ-hydroxy ketone it may undergo cyclization into a hemi-acetal configuration. The mechanism for the transformation of VI to IX involves two Wagner rearrangements

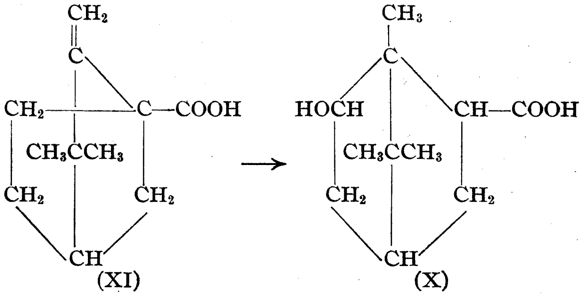



(X)

The dehydration of (VI) into (VIII) resembles the transformation of borneol into camphene



whereas that of (VIII) into (IX) is strictly analogous to the transformation[10] of camphenecarboxylic acid (XI) into (X).



Our hydroxycamphanecarboxylic acid (X), prepared by oxidation of (IX), was identical with Houben's acid (X), prepared from (XI).

Since these several cases have proven that ketones are the important rearrangement products of ethynylcarbinols, rather than aldehydes, serious doubt is cast on other similar cases wherein aldehydes are stated to be formed but wherein definite proof for the assertion is lacking. Obviously, the various non-discriminatory reactions of the "aldehydes" which appear in the literature (such as with the Grignard reagent, reducing agents, hydroxylamine or semicarbazide) should be reinterpreted on the basis of ketones.

Experimental Part

Preparation of Reagents.—Ethynylcyclohexanol, b. p. 74–76° (12 mm.), was prepared in 30% yield by Rupe's method, as modified by Hurd and Jones.[1] In the prepara-

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[10] Houben, *Ber.*, **59**, 2285 (1926).

tion of ethynylmethylphenylcarbinol, the directions of Rupe and Geisler[9] were modified by using benzene instead of ether. Instead of keeping the solution at ice temperature during the addition of the acetylene, it was kept refluxing gently. Also, the acetylene was led in before the sodium had dissolved. The yield of this carbinol, b. p. 85–90° (4 mm.) and m. p. 49°, was 13.5%. It was accompanied by about thrice the quantity of the pinacol of acetophenone.

Ethynylbornyl Alcohol VI.—One hundred grams of camphor dissolved in 600 cc. of dry benzene was placed in a 3-necked, liter flask to which was attached a long spiral reflux condenser, mercury stirrer and an inlet for acetylene. To this was added 16 g. of finely cut sodium. Then, while the solution was kept gently refluxing, acetylene was passed through for fifteen hours. After standing overnight, the solution was hydrolyzed with water and neutralized with hydrochloric acid. The solution was then steam distilled. The benzene layer was separated and treated with alcoholic silver nitrate, whereupon an abundant white crystalline precipitate formed. Its weight was 37 g. This was filtered, washed with alcohol and dried.

The silver salt was treated with an equal weight of ammonium thiocyanate in water solution. The insoluble layer was extracted with benzene, dried over calcium chloride and the benzene was evaporated. Sublimation attended efforts to distil the residue *in vacuo:* hence, the material was sublimed under reduced pressure. In all, 15.3 g. of ethynylbornyl alcohol was obtained having a m. p.[11] of 97–98°. This is a 13% yield.

Anal. (by Maxwell Pollack). Calcd. for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.42; H, 10.00.

Ethynylfenchyl Alcohol.—Similar directions were adapted for this synthesis. The chief difference from Rupe and Kuenzy's[12] published directions is the use of hot benzene instead of cold ether as the reaction medium, but it brought about a greatly improved yield. With their directions, reported to yield 8–10%, we obtained about a 7% yield. The modified directions listed below gave about a 29% yield.

Forty grams of finely cut sodium and 600 cc. of benzene were placed in the apparatus and the mixture was saturated with acetylene after which 200 g. of fenchone was added gradually. The solution warmed up to reflux temperature as the stream of acetylene was passed through. The total period of addition was forty-eight hours.

After standing for twelve hours, the solution was hydrolyzed with water and neutralized with hydrochloric acid. The solution was then steam distilled. The benzene layer was separated, dried and evaporated to a small volume under reduced pressure. (No difficulty due to sublimation was observed in this case.) The residue was treated with silver nitrate in alcoholic solution. An abundant white crystalline precipitate formed. This salt was filtered, washed with alcohol, dried, treated with an equal weight of ammonium thiocyanate (in water) and then steam distilled. The insoluble layer was separated, dried over sodium sulfate and distilled. A total of 67.4 g. of ethynylfenchyl alcohol, b. p. 90° (12 mm.), was obtained.

Rearrangements

Ethynylcyclohexanol.—Rupe's procedure, that of heating the compound with formic acid, was followed except for minor variations. The product of rearrangement (57% yield) boiled at 60–64° (4 mm.). As reported by Rupe, this material gave a positive test with Schiff's reagent. Its semicarbazone melted at 220–221° after three crystallizations from alcohol.

1-Acetyl-1-cyclohexene (III).—This compound was made from cyclohexene (86 g.), acetyl chloride (78 g.), carbon disulfide (600 cc.) and aluminum chloride (133 g.) by Darzens' method.[13] The yield of (III), b. p. 195–202°, was 26 g. or 21%. Its semicarbazone melted at 220–221°. A mixed melting point determination of this semicarbazone and that of the previous paragraph was 220–221°.

Behavior of Ethynylmethylphenylcarbinol toward Formic Acid.—Analogous to the yield of 1 g. of product, b. p. 122–130° (12 mm.), from 10 g. of the carbinol which was reported by Rupe and Giesler,[9] we obtained 1.7 g. (b. p. 100–110° at 6 mm.) from 12 g. The residue was a dark red tar. The liquid product reacted positively toward Schiff's reagent. Its semicarbazone melted at 201° (Rupe and Giesler reported 201–202°). A mixed melting point determination with authentic acetophenone semicarbazone, m. p. 201°, was 201°.

Further evidence that this material was acetophenone, not β-phenylcrotonaldehyde (IV) as postulated by Rupe and Giesler, was its behavior on ozonolysis. Acetophenone (unused) and benzoic acid, m. p. 121°, were the products obtained. The latter would not be expected from (IV).

To make sure that acetophenone did not preëxist in the carbinol taken for rearrangement, more of the carbinol was prepared and purified rigorously. A portion of the product, collected at 83–86° (6 mm.), was treated with alcoholic silver nitrate solution. The yellow precipitate was collected on a filter, washed repeatedly with alcohol, then dried. Part of the salt was lost when it exploded violently. Equal weights of the salt and of ammonium thiocyanate were warmed in a flask with water to recover the ethynylcarbinol. The insoluble layer was extracted with benzene, dried, distilled, and twice recrystallized from petroleum ether. The m. p. was 49° and no semicarbazone was obtainable from it.

This pure ethynylmethylphenylcarbinol (4.4 g.) was heated with 50 cc. of 90% formic acid until spontaneous reaction occurred. When this had subsided it was refluxed for thirty minutes. Then the solution was neutralized with alkali and the insoluble layer extracted with benzene. Distillation yielded 0.5 g. at 100–110° (6 mm.) which, as before, was acetophenone; semicarbazone, m. p. and mixed m. p., 201°.

Rearrangement of Ethynylbornyl Alcohol (VI).—Ten grams of (VI) was placed in an all-glass refluxing apparatus with 60 cc. of 90% formic acid. The mixture was heated until a spontaneous reaction took place. The solution turned first to a red then to a deep brown color. Heating was continued for an additional hour. The solution was

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[11] After the completion of the present study notice appeared of the synthesis of this compound by Dulou, *Bull. inst. pin*, **178**, 197 (1934); *C. A.*, **29**, 2945 (1935). Dulou's compound melted at 85° whereas ours was 98°.

[12] Rupe and Kuenzy, *Helv. Chim. Acta*, **14**, 708 (1931).

[13] Darzens, *Compt. rend.*, **150**, 707 (1910); Wallach, *Ann.*, **360**, 46 (1908).

neutralized with sodium hydroxide. The insoluble layer was extracted with benzene, dried over calcium chloride and then distilled under reduced pressure. A total of 7.5 g. (75% yield) of the rearranged product was obtained; b. p. 96–98° (6 mm.); $n^{24}D$ 1.4733. The substance gave a positive iodoform reaction, indicative of the $-COCH_3$ group. Schiff's reagent required considerable time for a slight color change. When 0.5 g. of this material in 50 cc. of alcohol was refluxed for five hours with freshly prepared silver oxide, no acid was obtainable on working up the products. Crystallization of this material was a difficult matter but it was found that solidification set in after about two weeks at room temperature. Recrystallization of this product from petroleum ether yielded crystals which melted at 77–78°. Analysis was satisfactory for 2-acetyl-6-hydroxycamphane (IX).

Anal. (by M. Pollack). Calcd. for $C_{12}H_{20}O_2$: C, 73.41; H, 10.27. Found: C, 73.43; H, 10.03.

Ozonization of 2-Acetyl-6-hydroxycamphane.—Eighty cc. of carbon tetrachloride was used as solvent for 4.14 g. (0.021 mole) of (IX) and 62.3 liters of an 8–10% ozone mixture was run in during twenty hours. The ozonide was hydrolyzed by warming on the steam-bath with an equal volume of water. There was formed 0.040 mole of acidic material (97.0 cc. of 0.4170 *N* sodium hydroxide solution was required). The neutral aqueous solution was extracted twice with carbon tetrachloride, then concentrated and acidified with hydrochloric acid. A brown, viscous mass separated which, after three crystallizations from alcohol–water, yielded 2.8 g. (0.014 mole) of white, crystalline 6-hydroxy-2-camphanecarboxylic acid[14] (X), m. p. 221°.

Neut. eq. Calcd. for $C_{11}H_{18}O_3$, 198.2. Found: 198.8 (0.2649 g. required 12.20 cc. of 0.1091 *N* NaOH).

Anal. (semi-micro). Calcd.: C, 66.62; H, 9.15. Found: C, 66.62, 66.40; H, 9.07, 9.16. *Anal.* (macro, by M. Pollack). Found: C, 66.64; H, 9.02.

Semicarbazone.—This derivative, prepared in the usual manner from IX, melted at 202°. That it was the semicarbazide of 1-acetylcamphene (VIII), rather than of IX, was shown by analysis. Evidently a dehydration process occurs during semicarbazone formation.

Anal. Calcd. for $C_{13}H_{21}ON_3$: N, 17.88. Calcd. for $C_{13}H_{23}O_2N_3$: N, 16.60. Found (Dumas): N, 17.84, 17.81.

Summary

Rearrangement of ethynylcyclohexanol by hot formic acid yields 1-acetyl-1-cyclohexene, not cyclohexylideneacetaldehyde, since it is identical to the substance prepared from cyclohexene, acetyl chloride and aluminum chloride. Other evidence for the structure of the product is cited also.

No evidence could be found to support the statement in the literature that an isomeric aldehyde is produced from ethynylmethylphenylcarbinol by rearrangement with formic acid. Instead of β-phenylcrotonaldehyde, the product formed is acetophenone. The bulk of the product is a tar which probably arises *via* 2-phenylbutenone.

Ethynylbornyl alcohol, prepared from camphor, acetylene and sodium, undergoes rearrangement to 2-acetyl-6-hydroxycamphane. On oxidation, this substance yields 6-hydroxy-2-camphanecarboxylic acid. Improved directions are given for the synthesis of ethynylfenchyl alcohol.

EVANSTON, ILLINOIS RECEIVED OCTOBER 15, 1936

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[14] Houben, *Ber.*, **59**, 2285 (1926), reported a melting point of 216–220°.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Removal of HX from Organic Compounds by Means of Bases. III. The Rates of Removal of Hydrogen Bromide from Substituted N-Bromobenzamides and their Relative Ease of Rearrangement in the Presence of Alkali. The Hofmann Rearrangement

BY CHARLES R. HAUSER AND W. B. RENFROW, JR.

According to the most generally accepted mechanism for the Hofmann rearrangement of a bromoamide in the presence of alkali,[1] hydrogen bromide is removed to form an unstable univalent nitrogen compound which undergoes the rearrangement to give an isocyanate. Since it is possible to isolate the alkali salts, (RCONBr)Na, of certain bromoamides, the reaction apparently involves first, the removal of the hydrogen as a proton, followed by the release of bromide ion and rearrangement of the molecule; this might be represented as follows

$$\mathrm{RCONHBr} \xrightarrow{+\mathrm{OH}^\ominus} \mathrm{RCONBr}^\ominus \xrightarrow{-\mathrm{Br}^\ominus} (\mathrm{RCON}) \longrightarrow \mathrm{RCNO}$$

We have taken the view that the rate determining step of this process is the release of bromide ion from the negative ion of the salt, and that the rearrangement, if it is a separate step, occurs rela-

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[1] See especially Porter, "Molecular Rearrangements," The Chemical Catalog Co., New York, 1928, pp. 13–30.

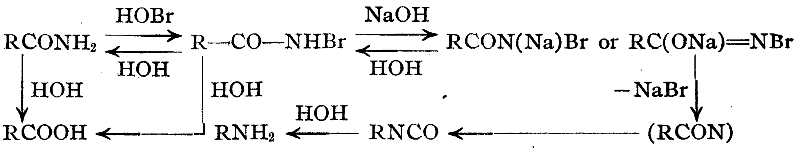
tively rapidly as the molecule is stabilized.[2] On this basis the ease of rearrangement[3] of a bromoamide in the presence of alkali would be dependent upon the rate of removal of bromide ion. As a possible test for this hypothesis, a study has been made of the rates of decomposition of the sodium salts of a series of meta and para substituted bromobenzamides. It seemed reasonable to expect that if this view were correct then an inverse relationship should exist between the rates of decomposition of these salts and the dissociation constants of the corresponding carboxylic acids. Linear relationships have been reported recently between the rates of certain reactions and the dissociation constants of the corresponding acids.[4] An inverse relationship should be expected in the case of the bromoamide salts since, in their decomposition, bromine is released as a negative bromide ion, whereas, in the dissociation of an acid, hydrogen is removed as a positive ion, *i. e.*, as a proton; this relationship has been verified for certain meta and para substituted bromobenzamides.

Experimental

Preparation of Bromobenzamides.—These compounds were prepared by a modification of the method by which Hoogewerff and van Dorp[5] prepared bromobenzamide and certain of its derivatives. Ten grams of pure, finely pulverized amide was added to 150 cc. of an ice-cold solution of sodium hypobromite, freshly prepared from 14.4 g. (0.09 mole) of bromine, and 9.0 g. (0.23 mole) of sodium hydroxide. After shaking for ten minutes, the mixture was filtered rapidly with suction into a cold solution of 9 cc. of glacial acetic acid in 25 cc. of water containing crushed ice. The bromoamide which precipitated was filtered off and washed thoroughly with water. The following conditions were found best for recrystallizing the various bromobenzamides used in this work. Bromobenzamide and the *p*-methyl derivative were dissolved in boiling chloroform, petroleum ether (b. p. 60–70°) added until turbidity just disappeared, and the solution cooled; the *m*-bromo and *m*-chloro derivatives were dissolved in glacial acetic acid at 50–60°, water added until cloudiness just disappeared, and the solution cooled; the *m*-nitro derivative was dissolved in acetic acid at 80–85°, water or petroleum ether added and the solution cooled; the *p*-chloro derivative was recrystallized from hot (70–80°) 50% aqueous acetic acid, the *p*-nitro derivative from boiling glacial acetic acid, and the *o*-chloro derivative from a boiling mixture of two parts of carbon tetrachloride to one of chloroform. The *p*-methoxy derivative was dissolved in a 5% solution of sodium hydroxide containing ice, and filtered into dilute acetic acid and ice. The yields of pure products obtained were 40–70% of the theoretical quantities. They should be kept cold, away from light.

For analysis the bromobenzamides were dissolved in glacial acetic acid, excess potassium iodide added, the solution diluted with water to about 150 cc., and the liberated iodine titrated with sodium thiosulfate to the starch–iodide end-point. The analytical data for the bromobenzamides used in this work are given in Table I. These compounds melted with decomposition. Their approximate melting or decomposition points are given in Table I. These values were determined by immersing samples in a bath which was previously heated to within 5–10° of these temperatures and gradually heating the bath in the usual manner.

Products of Reactions of Bromobenzamides with Alkali.—Bromoamides readily dissolve in sodium hydroxide to form sodium salts[1,5] which release bromide ion and undergo rearrangement to isocyanates. In the presence of alkali, the latter are hydrolyzed to primary amines. Bromoamides may also undergo hydrolysis to form the corresponding acids. These reactions may be represented by the following scheme.



$$\begin{tikzcd}
\mathrm{RCONH_2} \arrow[r, shift left, "\mathrm{HOBr}"] \arrow[d, "\mathrm{HOH}"'] & \mathrm{R{-}CO{-}NHBr} \arrow[l, shift left, "\mathrm{HOH}"] \arrow[r, shift left, "\mathrm{NaOH}"] \arrow[dl, "\mathrm{HOH}"] & & \mathrm{RCON(Na)Br\ or\ RC(ONa){=}NBr} \arrow[ll, shift left, "\mathrm{HOH}"] \arrow[d, "-\mathrm{NaBr}"] \\
\mathrm{RCOOH} & \mathrm{RNH_2} & \mathrm{RNCO} \arrow[l, "\mathrm{HOH}"'] & \mathrm{(RCON)} \arrow[l]
\end{tikzcd}$$

TABLE I

ANALYTICAL DATA AND MELTING POINTS OF SUBSTITUTED BROMOBENZAMIDES

Substituent	M. p. (dec. T), °C.	Active bromine, % Calcd.	Active bromine, % Found
p-CH_3	131–133	37.34	37.13
o-Cl	104–105	34.09	33.90
H	129–131	39.96	39.72
p-Cl	170–174	34.09	34.05
m-Br	122–126	28.65	28.34
m-Cl	102–105	34.09	34.00
o-NO_2	170–176	32.62	32.38
m-NO_2	173–176	32.62	32.44
p-NO_2	198–202	32.62	32.30

At 30° in the presence of a large excess of alkali, the yields of amine obtained from the bromobenzamides studied in this investigation, with the exception of the nitro derivatives, were 90% or better, whereas the yields of the corresponding acids were less than 5% (see Table IV). The meta and para nitro derivatives, however, gave 25 and 46% yields of the corresponding acid, those of the

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[2] In this connection see especially, Whitmore, THIS JOURNAL, **54** 3281 (1932); Wallis and Whitmore, *ibid.*, **56**, 1427 (1934).

[3] Jones and co-workers[1] assumed that the ease of rearrangement of this type is dependent upon the tendency for the radical R, in the univalent nitrogen derivative, to exist as a free radical, and they presented certain evidence to support this hypothesis. Recently, Wallis and co-workers [THIS JOURNAL, **55**, 1701, 2598 (1933); and Bell, *J. Soc. Chem. Ind.*, **52**, 584 (1933)], have presented evidence that R does not actually exist as a free radical during the Hofmann rearrangement.

[4] (a) Hammett and Pfluger, THIS JOURNAL, **55**, 4079 (1933); Hammett, *Chem. Rev.*, **17**, 125 (1935); (b) Dippy and Watson, *J. Chem. Soc.*, 436 (1936).

[5] Hoogewerff and van Dorp, *Rec. trav. chim.*, **8**, 173 (1889); see also, *ibid.*, **6**, 373 (1887). In agreement with our results these workers have shown that the potassium salts of *m*- and *p*-nitrobromobenzamides are more stable than the salt of bromobenzamide.

amines being correspondingly smaller. The relatively low yields of amines obtained in these cases may be explained by the fact that the rate of rearrangement of these compounds is greatly retarded by the presence of the nitro group (see Table IV), whereas the rate of hydrolysis is probably accelerated. It is of interest that the rearrangement apparently has a higher temperature coefficient than the hydrolysis. A 90% yield of *p*-nitroaniline was obtained when *p*-nitrobromobenzamide was dissolved in alkali solution at the temperature of the boiling water-bath (96–100°), whereas a yield of amine of only 48% was obtained at 30°. This point should be considered in the preparation of amines by this reaction.

The yields of amine and acid given in Table IV have been determined under the conditions used in the rate measurements described below. These products were isolated according to the following procedure.

The pure bromoamide (0.005 mole) was dissolved in 100 cc. of 1.0 molar carbonate-free sodium hydroxide solution at 30 ± 0.02°, and kept at this temperature until the mixture no longer contained active bromine. In order to convert any unchanged isocyanate into primary amine, the mixture was acidified with hydrochloric acid and heated on the water-bath for an hour. It was then cooled and extracted with three 25-cc. portions of ether. Organic acid mixed with a very small amount of neutral tarry material was obtained from the dried[6] ether extracts by evaporation of the solvent. The primary amine was obtained from the aqueous solution by making it alkaline and extracting it with three portions of ether. Liquid amines were isolated as their hydrochlorides by passing dry hydrogen chloride into their dried ether solutions. The organic acids and solid amines were identified by their melting points and in most cases by mixed melting points with authentic specimens.

Relative Stabilities of the Sodium Salts of Bromobenzamides.—Van Dam and Aberson[7] have studied the rate of decomposition of bromobenzamide in various concentrations of alkali. With an equivalent of alkali a colored precipitate formed within a short time, interfering with the titration; benzoylphenylurea was isolated from the reaction mixture. Under these conditions we have been able to obtain a yield of aniline of only 30% of the theoretical amount. Van Dam and Aberson[7] showed that in the presence of an excess of alkali the rate was dependent not only on the concentration of bromobenzamide but also on that of the alkali, being approximately proportional to the concentration of alkali when twenty to forty equivalents of the latter to one of the bromoamide were used.[8] We have obtained 94–95% yields of aniline using 10, 20 or 40 equivalents of alkali to one of bromobenzamide. In this investigation therefore, the rates of decomposition of substituted bromobenzamides were determined in the presence of a large excess (20 to 1) of alkali, using the same molar concentrations of reactants in all cases.

The course of the reaction of a 0.05 molar bromoamide solution in 1.0 molar sodium hydroxide at 30 ± 0.02° was followed by titrating samples for active bromine in the usual manner. Since the reaction is first order with respect to the bromoamides, velocity constants have been calculated from the first order rate of reaction equation

$$K = \frac{2.303}{t} \log \frac{a}{a - x}$$

where t is in minutes. Two sets of measurements have been made with each bromoamide, the data and velocity constants with a representative compound being given in Table II. The average values of velocity constants K, calculated for 25–95% decomposition of the bromoamides are arranged in decreasing order in Table IV. With the exceptions of the *p*-methoxy and the nitro derivatives, these values are reproducible to within 1–3%. Under the conditions used the *p*-methoxy compound[9] decomposed too rapidly (95% within five minutes) to measure accurately. The values of K calculated for the *o*-, *m*- and *p*-nitro derivatives were not constant but increased steadily from 0.00105–0.00174, 0.000556–0.000988 and 0.000823–0.000974, respectively. Mean values are recorded in Table IV merely to illustrate their relative stabilities. It is to be noted that in these cases considerable hydrolysis occurred.

Velocity constants for the sodium salts of bromobenzamide and of *p*-methyl- and *m*-chlorobromobenzamides have been measured at two or three temperatures, and the heats of activation

TABLE II

RATES OF DECOMPOSITION OF *m*-CHLOROBROMOBENZAMIDE ($0.05\ M$) IN $1.0\ M$ NaOH AT 30°

Run no. 1 Time, min.	Cc. $Na_2S_2O_3$ 0.02 N	K	Run no. 2 Time, min.	Cc. $Na_2S_2O_3$ 0.02 N	K
0	44.60	0.00621[a]	0	47.85	0.00526[a]
12.75	41.19	.00573	14	44.45	.00555
37.75	35.92	.00571	35	39.40	.00565
63.25	31.08	.00571	65	33.15	.00567
100.75	25.07	.00571	111	25.50	.00566
130.75	21.13	.00571	169	18.40	.00566
309.25	7.60	.00571	221	13.70	.00566
	Average	.00571		Average	.00566

[a] Not averaged.

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[6] Anhydrous calcium sulfate (Drierite) was used.

[7] Van Dam and Aberson, *Rec. trav. chim.*, **19**, 318 (1900); Van Dam, *ibid.*, **18**, 408 (1899).

[8] It does not seem possible that this alkali effect could be due only to a shift in the equilibrium of the acid–base reaction between the bromoamide and alkali. Further studies in this connection are planned.

[9] This was the most unstable compound prepared. A product 90% pure was used for an approximate rate determination.

calculated. The results are given in Table III. It can be seen that the heat of activation for the *p*-methyl derivative is about one thousand calories less than that for bromobenzamide, whereas the value obtained for the *m*-chloro derivative is 400 cal. greater; this latter difference might be within the experimental error. This phase of the problem is being studied further.

TABLE III

HEATS OF ACTIVATION OF THE SODIUM SALTS OF BROMOBENZAMIDE AND CERTAIN OF ITS DERIVATIVES

Derivative	T_1	K_1	T_2	K_2	Q
p-Methyl	30	0.138	20	0.0301	27,000
p-Methyl	20	.0301	11.5	.00741	27,300
Bromobenzamide	30	.0461	20	.00942	28,200[a]
m-Chloro	45	.0536	30	.00569	28,600

[a] From the data reported by Van Dam and Aberson for bromobenzamide the heat of activation of 28,700 cal. has been calculated; see ref. 7.

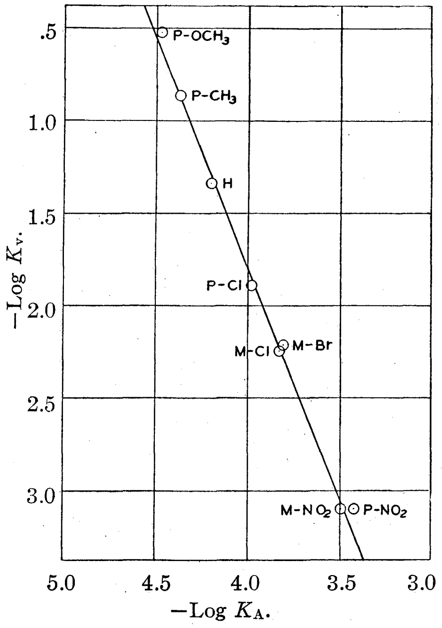

Fig. 1.

TABLE IV

RATES OF DECOMPOSITION OF SUBSTITUTED BROMOBENZAMIDES (0.05 *M*) IN 1.0 *M* NaOH AT 30° AND YIELDS OF PRODUCTS OBTAINED

Substituent	Monomolecular constant *K*	K_A of RCOOH[a] $\times 10^5$	Percentage yields Amine	Acid
p-CH_3O	0.3[b]	3.38	....	....
p-CH_3	.138	4.24	98	Trace
o-Cl	.0533	(114.)	....	....
H	.0461	6.27	95	2
p-Cl	.0130	10.5	94	5
m-Br	.00615	15.4	90	4
m-Cl	.00569	14.8	92	3
o-NO_2	.0013[c]	(700.)	....	....
m-NO_2	.0008[c]	32.1	70	25
p-NO_2	.0008[c]	37.6	48	46

[a] The dissociation constants listed here, with the exception of the one for *o*-nitrobenzoic acid, have been taken from the recent papers of Dippy and co-workers, see note 13. [b] An approximate value for the constant. In qualitative agreement with our results, Van Dam has previously reported that in the presence of potassium hypobromite, *p*-methoxybenzamide is decomposed more readily than benzamide; see ref. 7. [c] Not a constant; an average value only.

It can be seen from Table IV that the rates of decomposition of the salts of the meta and para substituted bromobenzamides at 30°, and presumably their ease of rearrangement,[10] are in general in the inverse order to the dissociation constants of the corresponding carboxylic acids.[11] When the logarithms of the rate constants[12] are plotted against the logarithms of the dissociation constants of the corresponding acids an approximately linear relationship is exhibited as shown in Fig. 1; the equation for the straight line is $\log K_v = -11.81 - 2.50 \log K_A$. The dissociation constants used here are the thermodynamic values recently reported by Dippy and co-workers.[13] If the values given in the "International Critical Tables" are used, the discrepancy between the *m*-chloro and *m*-bromo derivatives disappears but, on the whole, the linear relationship is not quite as good as that represented in Fig. 1.

It is considered that these results are in agreement with the hypothesis that the ease of rearrangement of a bromoamide in the presence of alkali is dependent upon the ease of release of bromide ion from the negative ion of the salt. It can be seen from Table IV that the *o*-chloro and *o*-nitro derivatives are more unstable than would be anticipated from the dissociation constants of the corresponding acids; however, such lack of agreement between theory and experiment with ortho substituted compounds has been observed in other cases.[14]

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(10) This does not necessarily mean that the ease of rearrangement of the corresponding univalent nitrogen compounds, if they have an independent existence, would be in the same order; see note 3.

(11) In this connection it should be mentioned that certain hydroxy bromobenzamide derivatives are very unstable. McCoy, *Am. Chem. J.*, **21**, 116 (1899); see also ref. 7.

(12) See note (c) Table IV.

(13) Dippy and co-workers, *J. Chem. Soc.*, 1888 (1934); 343 (1935); 645 (1936).

(14) In this connection it is of interest to note that although the calculated dipole moments of *m*-, and *p*-chlorobenzoic acids can be correlated with their dissociation constants, apparently no correlation is found in the case of *o*-chlorobenzoic acid; dipole moment calculations seem to indicate that the latter should be weaker than benzoic acid, whereas actually it is much stronger; see Smallwood, THIS JOURNAL, **54**, 3048 (1932); see also ref. 4b.

The writers wish to thank Dr. Douglas G. Hill for suggestions on the kinetics of these reactions.

Summary

1. The rates of decomposition of the sodium salts of a series of substituted bromobenzamides have been measured at 30°.

2. The rates of decomposition of the sodium salts of bromobenzamide and of *m*-chloro- and *p*-methylbromobenzamides have been measured at two or three temperatures and their heats of activation calculated.

3. It has been found that the relative rates of decomposition of certain meta and para substituted bromobenzamides at 30°, and presumably their relative ease of rearrangement in the presence of alkali, are inversely related to the dissociation constants of the corresponding carboxylic acids.

4. These results are considered to be in agreement with the hypothesis that the ease of rearrangement of a bromoamide in the presence of alkali is dependent upon the ease of release of bromide ion from the negative ion of the alkali salt.

5. It has been found that in the presence of excess alkali at 30°, *p*-nitrobromobenzamide gives approximately as much *p*-nitrobenzoic acid by hydrolysis as *p*-nitroaniline by rearrangement; at 96–100°, however, a 90% yield of *p*-nitroaniline is obtained.

DURHAM, N. C. RECEIVED AUGUST 12, 1936

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XXVI. The Properties of Spruce Lignin Extracted with Formic Acid

BY GEORGE F. WRIGHT AND HAROLD HIBBERT

The recent publications by Freudenberg and co-workers[1] and by Staudinger and Dreher,[2] in which they describe the extraction of spruce wood meal with formic acid, anticipate a current investigation in this Laboratory. Although this study is not yet complete it seems advisable to present a preliminary account of the work.

Considerable doubt exists as to the reliability of any known extraction process for isolating *unchanged* lignin from wood, and it seems preferable to consider an extractant as the first reagent in a series of reactions intended to prove structure. As one of a series of such extractants, so regarded, it has been found that boiling formic acid removes from resin- and soluble-carbohydrate-free spruce wood meal 17% of its weight in the form of methoxyl-containing material. Because of partial demethoxylation this process yields lignins of comparatively low methoxyl content (12–14%) but it possesses the advantages of: (a) rapidity and convenience of extraction, and (b) isolation of extracts readily soluble in many organic solvents. Thanks to this ease of solubility, it has been found possible to effect a separation of the isolated lignin into five fractions by precipitation of chloroform, acetone and aqueous acetone solutions into ether and also petroleum ether (Table I). This fractionation is undoubtedly incomplete; indeed, subsequent experiments show that the fractions are still complex. Nevertheless, examination of these partially separated products shows a definite trend in chemical and physical properties undoubtedly characteristic of the individual substances that comprise the isolated mixture called lignin.

The behavior of two functional groups has been examined in this study, namely, (a) reactions of the hydroxyl and (b) reactions of the carbonyl group. The suitable solubility of formic acid lignin has permitted the use of the Grignard machine[3] for simultaneous determination of both groups. These analyses have been supplemented by appropriate methoxylations and tosylations. The results (Table I) show two interesting facts: (i) the native lignins contain small amounts of non-enolizable carbonyl groups; (ii) the more soluble, and therefore simplest, fractions, have *higher hydroxyl* and *lower methoxyl* values than their more complex, insoluble analogs. This decrease in hydroxyl value with decreasing solubility suggests that increasing aggregation of

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(1) Freudenberg, Janson, Knopf and Haag, *Ber.*, **69**, 1415 (1936).

(2) Staudinger and Dreher, *ibid.*, **69**, 1729 (1936).

(3) Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927); Kohler and Richtmyer, *ibid.*, **52**, 3736 (1930).

TABLE I

EXTRACTION OF WOOD MEAL (40 GRAMS)[a]

	Extracting medium						Grignard machine analysis	
	Formic acid (95%) for 13 hr.		Formic acid (95%) for 6 hr.		Formic acid (80%) for 6 hr.			
Solubilities of product	Wt., g.	OCH_3, %	Wt., g.	OCH_3, %	Wt., g.	OCH_3, %	Active H per kg.	RMgX added per kg.
Chloroform–acetone–pet. ether soluble	0.16	...	..	...	..	...	...	...
Chloroform–acetone–ether soluble	.35	...	..	...	0.40	12.17	4.4	0.7
Chloroform soluble	.81	13.13	..	...	.64	13.38	4.6	.7
Acetone soluble	1.37	12.81	..	...	.92	13.42	3.5	.5
Soluble only in acetone–water	4.40	13.45	..	...	.19	14.15	3.0	.6
Total lignin	7.09	...	5.85	12.05	2.15	13.50	4.0	.6
Acetone–water insoluble	0.01	2.5	1.79	3.0	0.96	2.5		
Total water insoluble extract	7.10	...	7.64	...	3.11	...	...	...

[a] It should be noted that complete extraction of the lignin is favored by increased strength of formic acid and by longer heating; on the other hand, the amount of acetone–water insoluble extract decreases during the course of the extraction. An absolutely anhydrous medium should be avoided because of secondary reactions (presumably formylation) occurring during the extraction.

the lignin complex is associated with loss of hydroxyl. The question as to whether these more complex molecules exist pre-formed in the wood[1] or, alternatively, arise from some simpler type during the extraction process[4] would, at this time, seem to be of secondary importance as compared with elucidation of the structure of lignin as it comes to hand.

The small but consistent amount of Grignard reagent added by both native and substituted formic acid lignins confirms the previous claim[5] that lignin contains a carbonyl linkage. That this small value (about one-half carbonyl group per kilogram) is real is shown by treatment of the lignin with phenylmagnesium bromide; the phenylated lignin, thus produced, is no longer capable of adding methyl-magnesium iodide (Table II, expt. 8).

Analyses in the Grignard machine indicate that the *unfractionated* formic acid lignin contains about four hydroxyl groups per kilogram (Table I). This was confirmed by tosylation of the same material, four tosyl groups per kilogram being introduced. These four have been differentiated into phenolic and non-phenolic hydroxyl groups by methoxylation of the unfractionated lignin with diazomethane. Both the gas evolution and the final methoxyl value indicate that two out of the four hydroxyl groups per kilogram are phenolic in character. While the reaction with diazomethane provides inconclusive evidence for distinguishing phenolic, enolic and carboxylic hydroxyls, the presence of labile enol is considered improbable because of the constancy of the carbonyl value found in all of the formic acid lignin derivatives; a keto-enolic equilibrium undoubtedly would be disturbed in the several methoxylation processes which were employed. With regard to a carboxylic linkage, methoxylation would increase the carbonyl value, since methyl esters usually react with two equivalents of Grignard reagent. Since no change in the carbonyl value was found (Table II, expt. 7) it would seem that the hydroxyl groups, reactive toward diazomethane, are phenolic in character.[6]

This amount of phenolic hydroxyl is rather larger than that observed with other lignins.[7] It is, however, significant that this increase corresponds closely with the difference in methoxyl value between the spruce lignin isolated by the Klason method[8] (17%) and the formic acid method (14%). This evidence indicates that the labile methoxyl (which is liberated as methyl formate) is attached in the lignin to phenolic hydroxyl.

It was somewhat surprising to find that native formic acid lignin contained only four hydroxyl groups per kilogram, since complete methoxylation should yield, correspondingly, a lignin containing only 24.6% methoxyl, while it has been found by many investigators[7,8] that "completely methoxylated lignin" contains about 32% OCH_3. Actually a single methoxylation of the formic acid lignin with dimethyl sulfate and sodium hydroxide gave a product containing 24–27% OCH_3 (Table II, expts. 3, 4, 5, 6). Furthermore,

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(4) Hilpert and co-workers, *Ber.*, **67**, 1551 (1934); **68**, 16, 371, 380 (1935).

(5) (a) Cross and Bevan "Researches on Cellulose, III (1905–1910)," Longmans, Green and Co., London, 1912; (b) Schrauth, *Z. angew. Chem.*, **36**, 149 (1923); (c) Klason, *Ber.*, **56**, 200 (1923); (d) Friedrich, *Monatsh.*, **46**, 31 (1925).

(6) The term phenolic refers to the non-labile enolic hydroxy grouping such as exists in phenol.

(7) Brauns and Hibbert, THIS JOURNAL, **55**, 4720 (1933).

(8) Harris, *ibid.*, **58**, 894 (1936).

TABLE II

REACTIONS AND ANALYSES OF LIGNINS

				Machine analyses before reaction							Machine analyses of product		
No.	Wt. of lignin used, g.	Type of lignin used in reaction	% OCH_3 before reaction	Solvent	Active H per kg.	RMgX added per kg.	Description of reaction	Solubilities of product	Yield of product, g.	% OCH_3 in product	Solvent	Active H per kg.	RMgX added per kg.
1	1	Unfractionated formic acid	13.50	Quinoline	4.0	0.6	Methn. with $(CH_3)_2SO_4$ and $NaHCO_3$	Soluble, alkali, chloroform	0.84	15.8			
1a	1	Product No. 1	15.8				Solution in 2% NaOH for 48 hr. acidification	Insoluble, chloroform, acetone Soluble, water–acetone					
2	1	Unfractionated formic acid	13.50	Quinoline	4.0	.6	Methn. with $(CH_3)_2SO_4$ and Na_2CO_3 Wash with 1% NaOH	Insoluble, alkali Partly sol. benzene, ethyl alcohol Soluble, chloroform, acetone	.83	20.72	Dioxane	3.3	0.6
3	1	Unfractionated formic acid	13.50	Quinoline	4.0	.6	Methn. with $(CH_3)_2SO_4$ and 20% NaOH in air	Partly sol. benzene, ethyl alcohol Sol. chloroform, acetone	.88	24.30			
3a	0.88	Product No. 3	24.30				Methn. with diazomethane	Partly sol. benzene	.44	24.30	Dioxane	4.2	0.3
3b	.2	Product No. 3a	24.30	Dioxane	4.2	.3	Treatment with CH_3MgI, shaken with aq. acetone and $(CH_3)_2SO_4$		.15				
4	1	Unfractionated formic acid	13.50	Quinoline	4.0	.6	Methn. with $(CH_3)_2SO_4$ and 20% NaOH under N_2	Partly sol. benzene	.97	23.22			
4a		Product No. 4	23.22				Separation by benzene solubility	Fract. 1, benzene-sol.		23.85			
								Fract. 2, benzene-insol.	.88	22.91			
4b	0.90	Product No. 4	23.22				Methn. with $(CH_3)_2SO_4$ and 30% NaOH under N_2	Sol. benzene, chloroform, acetic acid Insol. ethyl alcohol, ether, carbon disulfide	.85	25.28			
4c	0.85	Product No. 4b	25.28				Methn. with $(CH_3)_2SO_4$ and 30% NaOH under N_2		.65	28.44			
4d	.65	Product No. 4c	28.44				Methn. with diazomethane	Partly sol. xylene	.55	30.0	1:1 xylene dioxane	2.3	0.7
5	1	Chloroform soluble formic acid	13.13	Dioxane	4.6	.7	Acetylation with C_5H_5N + Ac_2O: methn. with $(CH_3)_2SO_4$ and 30% NaOH under N_2	Sol. benzene	.92	25.82			
6	1	Acetone soluble formic acid	12.81	Dioxane	3.5	.5	Acetylation with C_5H_5N + Ac_2O: methn. with $(CH_3)_2SO_4$ and 30% NaOH under N_2	Partly sol. benzene Sol. chloroform	.87				
6a	0.87	Product No. 6					Separation by solubility in hot benzene	Fract. 1, benzene-sol.	.28	26.83	Dioxane	3.0	0.5
								Fract. 2, benzene-insol.	.48	23.30			
7	1	Unfractionated formic acid	13.50	Quinoline	4.0	.6	Methn. with diazomethane	Partly sol. benzene, ethyl alcohol Sol. chloroform	.97	18.55	Dioxane	2.0	0.6
8	1	Formic acid chloroform–acetone–ether soluble	12.17	Quinoline	4.4	.7	Reaction with C_6H_5MgBr and $(CH_3)_2SO_4$	Fract. 1, sol. chloroform–ether, sodium bicarbonate	.05	14.71			
								Fract. 2, sol. chloroform–ether, 1% sodium hydroxide	.56	18.31	Dioxane	4.9	0.0
9		Methanol–H_2SO_4	21.0				Methn. with diazomethane			24.7	Dioxane	3.0	0.4
10	5	CH_3OH–HCl on methylated wood	33.2				Methn. with diazomethane		3.5	35.42	Xylene	0.9	0.6
11	3	Unfractionated formic acid	12.86	Quinoline	4.0	.6	Reaction with tosyl chloride and pyridine	Insol. alkali Partly sol. dioxane Sol. chloroform, pyridine	4.47	7.79	Quinoline	4.0	2.
12		Chloroform soluble glycol–HCl	16.08	Dioxane	4.1	.0	Repeated acetylation–methn. with $(CH_3)_2SO_4$ + NaOH			31.76	Dioxane	2.0	0.3
13		Unfractionated formic acid	12.86	Quinoline	4.0	.6	Solution 45 days in 1% NaOH–acidification	Insol. acetone Partly sol. dioxane Sol. acetone–water		11.98	Dioxane	12.5	0.0

analyses of these methoxylated products in the Grignard machine showed that the lignin still contained from 4 to 3 free hydroxyl groups per kg. (Table II, expts. 3, 4, 6). Calculations from these figures indicate that complete methoxylation should yield lignin containing 34.6–35.2% OCH_3. Accordingly, two further methoxylations were effected with dimethyl sulfate followed by treatment with diazomethane (Table II, expt. 4), the final methoxyl value being 30%. Further attempts are being made to increase the methoxyl content of this product containing 30% OCH_3 and 2.3 hydroxyl groups per kg. However, the futility of alkaline methoxylation as a criterion for the detection and estimation of hydroxyl groups can be seen from the fact that this lignin (OCH_3 30%) still contains sufficient free hydroxyl groups to yield methoxylated lignin containing 36% methoxyl, assuming these groups to be capable of methoxylation. It is thus apparent that repeated methoxylation increases the *potential* methoxyl number by about 1% (34.6–35.2 to 36%). An explanation of this peculiar behavior is furnished in the analysis of the native lignin which had been allowed to stand for forty-five days in 1% sodium hydroxide solution (Table II, expt. 13), during which period there was no absorption of atmospheric oxygen. The original hydroxyl number increased from 4 to 12.5 per kg. with an accompanying decrease of methoxyl from 12.86 to 11.98%. The calculated methoxyl value, upon addition of 4.25 moles of water per kilogram of lignin, is 11.96%, *viz.* 12.86 (10)/[1000 + (12.5–4)18/2]. In short, hydroxyl groups appear *de novo* upon treatment of the native lignin with alkali.[8a] It is noteworthy that if the entire non-methoxyl oxygen content of the formic acid lignin were converted to hydroxyl (by ring opening) the hydroxyl number as deduced from ultimate analysis[2] would likewise be 12.5 per kg.

In view of these surprising results, other lignins were examined for their hydroxyl content. The chloroform soluble fraction of glycol lignin[9] (OCH_3, 16.68%) was found to contain 4.1 hydroxyl groups per kg. (Table II, expt. 12) corresponding to a fully methoxylated value of 27.3%. Repeated treatment of this with diazomethane, followed by subsequent acetylation and dimethyl sulfate methoxylation gave a product containing 31.7% OCH_3 and this "completely methoxylated" derivative still contained two free hydroxyl groups. On the other hand, a methanol lignin (OCH_3, 24.7%) which had been methoxylated only with diazomethane and, therefore, had not been subjected to an alkaline treatment was found to contain three free hydroxyl groups per kilogram (Table II, expt. 9). A sample of the fully methoxylated methanol lignin (OCH_3, 32%) was not available but a methoxylated methanol lignin prepared from methoxylated wood meal[10] and further methoxylated with dimethyl sulfate and sodium hydroxide, followed by treatment with diazomethane, gave a product with 35.4% OCH_3 but still containing 0.9 free hydroxyl group per kilogram (Table II, expt. 10). All of these methoxylated lignins were free from sulfur.

It thus appears that *alkaline methoxylation is unreliable both as a measure of the hydroxyl groups originally present in the lignin and of complete methoxylation.* A few attempts to methoxylate formic acid lignin with dimethyl sulfate at controlled *p*H (Table II, expts. 1, 2) resulted in incomplete reaction; the work is being continued. The possibility that the active hydrogen determination gives false values, either because of demethoxylation or enolization, is improbable. Firstly, no type of demethoxylation involving gas formation with Grignard reagent under these conditions is known, although what may be a typical compound, pentamethylquercetin, was examined (Table III, expt. 1). Secondly, the appearance of enolic methoxyl must necessarily be accompanied by a corresponding decrease in carbonyl value, while actually the carbonyl value is constant within experimental error. Consequently the Grignard analysis is considered reliable for the estimation of hydroxyl groups in lignin.

Extended speculation concerning these newly synthesized hydroxyl groups must await additional experimental evidence. Obviously they could be formed either by addition of the elements of water to double bonds, or by splitting of oxygen rings. It is improbable that all such oxygen rings could be pyrones because of the

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(8a) The authors find it necessary to point out that additional work has failed to confirm the *quantitative* values thus obtained, although *qualitatively* the evidence supports the conclusions drawn. They are likewise in harmony with previous experimental work carried out by Jack Compton in these laboratories and to appear in the *Canadian Journal of Research*, January, 1937.

(9) King, Brauns and Hibbert, *Can. J. Research*, **B13**, 35 (1935).

(10) Brauns and Hibbert, *ibid.*, **B13**, 78 (1935); Compton, Greig and Hibbert, *ibid.*, **B14**, 115 (1935).

TABLE III

ANALYSES OF RELATED COMPOUNDS

Expt. no.	Substance	Solvent	Active hydrogen	RMgX added
1	Pentamethylquercetin, m. p. 148°	Xylene	0.1 per mole	0.8 per mole
2	Cellulose prepared from wood meal (extracted twice with phenol containing 1% concd. HCl and dried at 60° (20 mm.) for 3 hr.	Quinoline (suspension)	1.2 per kg.	0.6 per kg.
3	Oleic acid	Xylene	1.1 per mole	1.0 per mole
4	Isosafrole	Xylene	0.1 per mole	0.0 per mole

low carbonyl value found in the lignin. This does not exclude the presence of the more probable chromanol grouping.[11] The experimental results are contradictory concerning this possibility. Since the splitting of a chromanol ring necessitates formation of a phenolic hydroxyl group, an attempt was made to determine this by treating the previously dimethyl sulfate-alkali methoxylated lignin with diazomethane (Table II, expt. 3a) but no phenolic group was detected. On the other hand, when the same lignin, thrice dimethyl sulfate-alkali methoxylated, was treated with diazomethane an increase of about 1.5% OCH_3 was observed (expt. 4d). The reason for this discrepancy is being investigated. It is certain that hydroxyl formation takes place under exceedingly mild conditions (1% sodium hydroxide) but ethylene oxide or lactone rings cannot be involved because they would have been detected in the Grignard analysis of the native lignin in amounts corresponding to the subsequent hydroxyl increase, resulting from ring fission.

Likewise from the evidence submitted here it is not possible to designate the type of carbonyl function found in this lignin except that it probably is not an acyl group (lignin-OCOR) which would have been removed during methoxylation. Also the carbonyl group is probably not of an enolizable type. The latter reservation follows from its constant value throughout the methoxylation experiments. The carbonyl function is, however, destroyed by prolonged treatment with alkali (Table II, expt. 13). Finally it must be emphasized that this is a preliminary report of work in progress, the methods of which are to be refined in the interest of accuracy.

The authors wish to thank Dr. Saul M. Trister for aid in the experimental work.

Experimental

Preparation of Formic Acid Lignin.—A suspension of 40 g. of spruce wood meal (75 mesh) (previously extracted successively with a 1:1 alcohol–benzene mixture, then with water, and dried at 55° (30 mm.))[12] in 300 cc. of formic acid of various concentrations (Table I) was refluxed in different experiments for six to thirteen hours. After cooling the mixture was filtered by suction and washed with 100 cc. of cold 90% formic acid. The residual moist wood meal (vacuum dried, wt. 23–15 g. depending on duration of boiling) was further extracted for twenty-four hours with 100 cc. of dioxane and another twenty-four hours with 100 cc. of dioxane containing 1% concd. hydrochloric acid. Although this latter treatment decreased the weight of wood meal from 23 g. (vacuum dried at 55°) to 14.6 g., the evaporated extracts yielded only 0.23 g. of lignin. Evidently a large part of the cellulose is hydrolyzed in the process. The reflux condenser was maintained at 40° during the extraction and the uncondensed gases from the condenser were conducted through a dry-ice trap. The condensate was identified as methyl formate (b. p. 31.5°) and by test for methanol following alkaline hydrolysis.

The original formic acid solution, obtained by filtration from the residual wood meal, was evaporated almost to dryness at 25 mm. pressure and the residue washed with water to remove soluble carbohydrates[13] and filtered by suction. After thorough washing with water on the filter and drying by prolonged suction under a rubber dam, the water-insoluble portion was dissolved in 300 cc. of a 3:17 water–acetone mixture leaving a residue[13] which was removed either by suction filtration or centrifuging. The solution was evaporated to dryness (25 mm.), the drying process being facilitated by addition of chloroform. The residue was extracted with three 100-cc. portions of chloroform and the extract concentrated to 40 cc. (30 mm.) (solution A). The chloroform-insoluble residue was further extracted with three 50-cc. portions of acetone and then concentrated to 50 cc. (30 mm.) (solution B). Finally the acetone insoluble residue was dissolved completely in 110 cc. of the 3:17 water–acetone mixture (solution C). These three solutions (A, B and C) were each precipitated into tenfold volumes of ether and the precipitates removed by centrifuging. The chloroform–ether and acetone–ether solutions, containing some lignin, were concentrated to 20 cc. and precipitated into 200 cc. of petroleum ether (b. p. 30–50°). Evaporation of the centrifuged chloroform–ether–petroleum ether solution left a slight residue of odoriferous material. The results of this separation are shown in Table I.

Methoxylation of Lignin with Diazomethane.—One gram of lignin was dissolved in 15 cc. of dry dioxane. To

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[11] Russell, *Chem. Rev.*, **17**, 155 (1935).

[12] As could have been predicted by King and Hibbert, *Can. J. Research*, **B14**, 12 (1936), a fourfold extraction of the wood meal with 5% alkali had no effect on methoxyl, active hydrogen or carbonyl content of the extracted lignin.

[13] At present undergoing investigation.

this solution at 25° was added, at one time, 4 cc. of an ether solution of diazomethane prepared from 0.5 cc. of nitrosomethylurethan. After five hours the gas evolution according to second order reaction rate ceased, about 48 cc. having been evolved. The solution was allowed to stand overnight, evaporated to dryness (30 mm.) and redissolved in benzene or acetone according to its solubility. The solution was centrifuged to remove diazomethane polymer and then precipitated into a tenfold volume of ether, the yield of centrifuged, ether-washed lignin dried at 60° (20 mm.) being 0.9–1.0 g.

Methoxylation of Lignin with Dimethyl Sulfate.—One gram of lignin was dissolved in a mixture of 40 cc. of acetone and 10 cc. of water. The solution was stirred under nitrogen while 3.8 cc. (0.09 mole) of dimethyl sulfate and 0.05 mole of the desired alkaline reagent were added simultaneously, the alkali being maintained constantly in excess during a period of ninety minutes and the solution stirred for a further thirty minutes. It was then diluted to 200 cc. with water, and acetic acid added until the suspension gave an acid reaction to litmus paper. At this point precipitation always occurred. The precipitated product was removed by extraction with chloroform, and the chloroform solution washed with 1% sodium hydroxide. In some cases it was found advisable to supplement this alkaline wash with an acid wash using 1% acetic or hydrochloric acid since chloroform soluble sodium lignates have been encountered. The washed chloroform solution was dried by evaporation at 25° (30 mm.) and the dried solution precipitated subsequently into a tenfold volume of ether or petroleum ether (b. p. 30–50°). The precipitated lignin was washed with a fresh portion of the precipitating reagent and dried at 60° (20 mm.). Yields were 0.9–1.0 g. as compared with yields of 0.8–0.9 for similar reactions carried out in air.

Tosylation of Lignin.—A solution of 3 g. of lignin and 5 g. of tosyl chloride in 50 cc. of dry pyridine was allowed to react for three days at room temperature and then added in a fine stream to 800 cc. of water containing 20 g. of potassium bicarbonate. After five hours' subsequent stirring, the precipitate was filtered by suction and dried (30 mm.). It was insoluble in alkali. A solution of the crude material in 100 cc. of chloroform was precipitated into 800 cc. of ether. The centrifuged, ether washed product was dried at 60° (20 mm.); weight, 4.47 g. The calculated yield, assuming esterification of four hydroxyl groups and addition of two molecules of water per kilogram is 4.96 g. The methoxyl content of this assumed compound would be 7.9% OCH_3. Found: OCH_3, 7.8%. One gram of the product when treated with phenylmagnesium bromide and subsequently oxidized with 1% potassium permanganate yielded 0.02 g. of sublimed benzoic acid.

Grignardization of Formic Acid Lignin.—A solution of 1 g. of chloroform–ether soluble lignin (containing 12.17% OCH_3 and 4.4 active hydrogen per kg.) in a mixture of 50 cc. ether and 50 cc. of dioxane was stirred under nitrogen while 20 cc. (0.021 mole) of phenylmagnesium bromide solution in ether was added over a ten-minute period. The reaction mixture was refluxed for two hours and allowed to stand overnight. Next day a solution of 4.75 cc. (0.05 mole) of dimethyl sulfate in 10 cc. of ether was added dropwise to the stirred reaction mixture in order to increase the lignin solubility by methoxylation. After three hours of refluxing the reaction was left overnight. Next morning the mixture was poured into 0.5% hydrochloric acid. The ether layer was diluted with chloroform, separated from the aqueous layer, and washed once with sodium bicarbonate solution and thrice with 1% sodium hydroxide in water. The acidified aqueous solutions were extracted thrice with chloroform. These solutions after drying by vacuum evaporation were precipitated into a tenfold volume of petroleum ether (b. p. 30–50°): yield of vacuum-dried product from the bicarbonate extract, 0.05 g.; OCH_3, 14.75%; yield of vacuum-dried product from the sodium hydroxide extract, 0.56 g.; OCH_3, 18.31%.

The reaction products so obtained were analyzed for methoxyl content (micro)[14] and for active hydrogen and carbonyl in the Grignard machine. The solution medium for this latter determination was either xylene, quinoline or dioxane (5 cc. in quantity), the latter two being conveniently purified by distillation from methylmagnesium chloride or sodium–benzophenone. Because of the volatility of dioxane on the boiling water-bath it was necessary to cool the outlet of the reaction flask during the heating period of fifteen minutes. The analyses together with yield and differentiating solubilities of the reaction products are summarized in Tables II and III.

Summary

1. The extraction of spruce wood meal with boiling formic acid is described.

2. A comparison of active hydrogen determinations with the results of alkaline methoxylation throws doubt on the hitherto assumed reliability of the latter as an agent for the proof of lignin structure.

3. The presence of carbonyl in lignin is confirmed.

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[14] The micromethoxyl method is admirably suited for the methoxyl determination of lignin because the divergence of duplicate analyses informs the experienced analyst as to the homogeneity of his sample. One-tenth of the amount of phenol recommended by Clark [THIS JOURNAL, **51**, 1979 (1929)] for the semi-micromethoxyl determination is employed.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Quinoline. I. Nupercaine Analogs. I

BY M. E. SMITH AND C. B. POLLARD

During the last few years, as a result of attempts to find new local anesthetics, a number of substituted 2-alkoxycinchoninamides have been prepared, of which nupercaine, N-diethyl-N′-(2-*n*-butoxycinchoninyl) ethylenediamine, is perhaps the best known. It has seemed advisable to extend this work to include certain piperazine and morpholine compounds.

In this investigation, 2-chlorocinchoninyl chloride was prepared by the method of Mulert,[1] except that purified commercial heptane (b. p. 93–97°) was used instead of ligroin to extract the product, and the hot heptane solution was filtered through a suction filter instead of being used in a Soxhlet extraction apparatus. 2-Chlorocinchoninyl chloride was treated with piperazine, N-phenylpiperazine, and morpholine to give N,N′-bis-(2-chlorocinchoninyl)-piperazine, N-phenyl-N′-(2-chlorocinchoninyl)-piperazine, and N-(2-chlorocinchoninyl)-morpholine, respectively. N-Phenyl-N′-(2-chlorocinchoninyl)-piperazine was treated with a number of sodium alcoholates to give several N-phenyl-N′-(2-alkoxycinchoninyl)-piperazines. The methoxy and ethoxy derivatives of N-(2-chlorocinchoninyl)-morpholine were prepared similarly.

The N-(2-ethoxycinchoninyl)-morpholine compound exhibited pronounced anesthetic action when tested on the tongue.

Pharmacological studies of these compounds are now being made under the direction of Dr. James C. Munch of John Wyeth and Brother. A report of these studies will appear at a later date.

Experimental

N,N′-Bis-(2-Chlorocinchoninyl)-piperazine.—A hot benzene solution of 22.6 g. (0.1 mole) of 2-chlorocinchoninyl chloride was added with stirring to 19.4 g. (0.1 mole) of melted piperazine hexahydrate. A white precipitate settled out. After this product had been washed well with water, acetone, alcohol and ether, it weighed 19.8 g. This compound was not appreciably soluble in any of the common organic solvents.

N-Phenyl-N′-(2-chlorocinchoninyl)-piperazine.—A hot benzene solution of 22.6 g. (0.1 mole) of 2-chlorocinchoninyl chloride was added with stirring to a mixture of 16.2 g. (0.1 mole) of N-phenylpiperazine in an aqueous solution of 5.3 g. (0.05 mole) of sodium carbonate. The resulting mixture was stirred for fifteen minutes and then allowed to stand for several hours. The product was filtered and washed with several portions of warm water, followed by a very small amount of acetone. The yield was 33.3 g. The compound was recrystallized twice from acetone before the melting point was determined. This compound is fairly soluble in alcohol and benzene, but is insoluble in water.

N-(2-Chlorocinchoninyl)-morpholine.—A hot benzene solution of 11.3 g. (0.05 mole) of 2-chlorocinchoninyl chloride was added while stirring to a mixture of 4.3 g. (0.05 mole) of morpholine in an aqueous solution of 2.7 g. (0.025 mole) of sodium carbonate. The resulting mixture was stirred for half an hour and then allowed to stand for several hours. The product was then filtered and washed with several portions of water, followed by a very small amount of acetone. The yield was 13.5 g. The product was recrystallized twice from 95% ethanol before the final

TABLE I

		M. p., °C. (corr.)	Yield, %	Formula	Analyses % N Calcd.	Found
1	N,N′-bis-(2-Chlorocinchoninyl)-piperazine	Not under 300	85	$C_{24}H_{18}Cl_2N_4O_2$	12.05	11.86
2	N-Phenyl-N′-(2-chlorocinchoninyl)-piperazine	189.2–190.2	95	$C_{20}H_{18}ClN_3O$	11.95	11.84
3	N-Phenyl-N′-(2-methoxycinchoninyl)-piperazine	149.5–150.2	Quant.	$C_{21}H_{21}N_3O_2$	12.10	12.02
4	N-Phenyl-N′-(2-ethoxycinchoninyl)-piperazine	154.0–154.5	Quant.	$C_{22}H_{23}N_3O_2$	11.63	11.34
5	N-Phenyl-N′-(2-*n*-propoxycinchoninyl)-piperazine	102.8–103.3	52	$C_{23}H_{25}N_3O_2$	11.20	11.00
6	N-Phenyl-N′-(2-isopropoxycinchoninyl)-piperazine	116.2–117.2	66	$C_{23}H_{25}N_3O_2$	11.20	11.00
7	N-Phenyl-N′-(2-*n*-butoxycinchoninyl)-piperazine	77.2–78.2	54	$C_{24}H_{27}N_3O_2$	10.80	10.67
8	N-Phenyl-N′-(2-alloxycinchoninyl)-piperazine	129.5–130.5	50	$C_{23}H_{23}N_3O_2$	11.26	11.06
9	N-Phenyl-N′-(2-beta-methoxyethoxycinchoninyl)-piperazine	91.6–92.3	41	$C_{23}H_{25}N_3O_3$	10.74	10.51
10	N-Phenyl-N′-(2-(N-phenyl-piperazino-N′-beta-ethoxy)-cinchoninyl)-piperazine	134.7–135.2	90	$C_{32}H_{35}N_5O_2$	13.43	13.18
11	N-(2-Chlorocinchoninyl)-morpholine	173.6–174.4	Quant.	$C_{14}H_{13}ClN_2O_2$	10.13	9.97
12	N-(2-Methoxycinchoninyl)-morpholine	134.0–134.9	65	$C_{15}H_{16}N_2O_3$	10.29	10.10
13	N-(2-Ethoxycinchoninyl)-morpholine	69.0–69.8	56	$C_{16}H_{18}N_2O_3$	9.79	9.47

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[1] Mulert, *Ber.*, **39**, 1901–1908 (1906).

melting point was determined. This compound is fairly soluble in acetone and benzene, but is insoluble in water.

N-Phenyl-N′-(2-alkoxycinchoninyl)-piperazines.—A hot solution of 8.8 g. (0.025 mole) of N-phenyl-N′-(2-chlorocinchoninyl)-piperazine in 140 ml. of benzene was added to a solution of 1.0 g. of sodium dissolved in 25 ml. of the appropriate alcohol, and the resulting mixture was refluxed four to fifty hours, after which it was filtered free from sodium chloride. In the cases of the methyl, ethyl, propyl and allyl compounds, the filtrate was evaporated to dryness, washed with water and recrystallized from 95% ethanol. In the cases of the others, the filtrate was washed with water and then evaporated to an oil, which was then dissolved in ethanol. Crystals eventually appeared from these alcoholic solutions, although with difficulty in some cases. All of the compounds were crystallized again from ethanol before their melting points were determined. These compounds are fairly soluble in acetone and benzene, but are insoluble in water.

N-(2-Alkoxycinchoninyl)-morpholines.—A hot solution of 5.5 g. (0.02 mole) of N-(2-chlorocinchoninyl)-morpholine in 50 ml. of benzene was added to a solution of 1.0 g. of sodium dissolved in 50 ml. of the appropriate alcohol. This mixture was refluxed for four hours, filtered and then evaporated to a solid. This was washed with water and then dissolved in ethanol. The crystals which later appeared were again crystallized before the melting points were determined.

A summary of the new nupercaine analogs is shown in Table I.

Summary

1. Thirteen new quinoline compounds analogous to nupercaine have been prepared and characterized.

2. At least one of these compounds has anesthetic properties.

3. Pharmacological studies of these compounds are now under way under the direction of Dr. James C. Munch of John Wyeth and Brother.

4. Work on these series of compounds is being continued in this Laboratory.

GAINESVILLE, FLA.

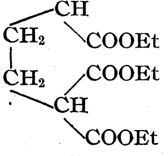
RECEIVED NOVEMBER 16, 1936

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

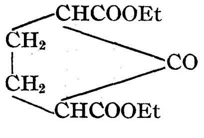
The Reaction of Certain Monosubstituted Malonic Esters and Methylene Dimalonic Esters with Sodium Ethoxide

BY J. R. ROLAND AND S. M. MCELVAIN

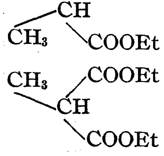
The fact that ethylene dimalonic ester (I) undergoes intramolecular condensation to give a dicarbethoxycyclopentanone[1] (II), led to the expectation that two molecules of methylmalonic ester (III), on account of their similarity to I in structure, should condense intermolecularly. As a matter of fact, such an intermolecular condensation of monosubstituted malonic esters had been predicted by Dieckmann[2] on the basis of his interpretation of the mechanism of the acetoacetic ester condensation. Later, however, Dieckmann and Kron[3] mentioned briefly in a footnote the failure of methylmalonic ester to undergo this condensation.



I



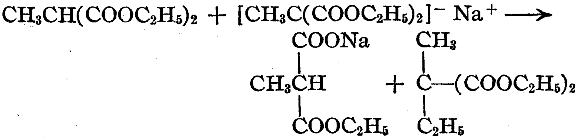
II



III

In view of this reported failure to realize an intermolecular condensation of III, it seemed worth while to ascertain what products, if any, result from the reaction of sodium ethoxide and methylmalonic ester. Of course the first product formed from these reactants is the sodium enolate of methylmalonic ester and an equivalent of alcohol. When the latter is removed by distillation the reactants remaining are this enolate and the excess methylmalonic ester. Such enolates are, therefore, the real condensing agents when such an ester as I is condensed.

When the sodium enolate of methylmalonic ester was heated at 140–160° with an excess of the ester, the reaction products isolated were monoethylmethylmalonate, methylethylmalonic ester and α-methylbutyric ester. The first two of these products are the result of the alkylation of the enolate by methylmalonic ester,[4] thus



$$CH_3CH(COOC_2H_5)_2 + [CH_3C(COOC_2H_5)_2]^- Na^+ \longrightarrow \underset{COOC_2H_5}{\overset{COONa}{CH_3CH}} + \underset{C_2H_5}{\overset{CH_3}{C}}\text{—}(COOC_2H_5)_2$$

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[1] Meincke, Cox and McElvain, THIS JOURNAL, **57**, 1133 (1935). *Cf.* also the condensation of the homologous trimethylene dimalonic ester [Guha and Seshadriengar, *Current Sci.*, **3**, 20 (1934)].

[2] Dieckmann, *Ber.*, **33**, 2678 (1900).

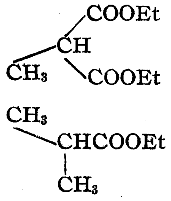
[3] Dieckmann and Kron, *ibid.*, **41**, 1260 (footnote 1) (1908).

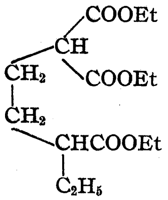
[4] *Cf.* Walter and McElvain, THIS JOURNAL, **57**, 1891 (1935).

The α-methyl butyric ester results from the decarboxylation of the methylethylmalonic ester. At lower temperatures (100–120° and 50–60°) this alkylation reaction did not occur and the only product under these conditions was due to the hydrolysis of the enolate[5] when the reaction mixture was worked up, since none of it was obtained when the reaction mixture was decomposed with dry hydrogen chloride. Apparently, therefore, the only reaction which methylmalonic ester shows with sodium ethoxide at 140–160° is self alkylation, and this reaction takes place to the extent of 72% of the theoretical.

It seemed necessary to determine whether or not this alkylation reaction was preventing any acetoacetic ester condensation of the malonic ester from taking place. This was done by using isopropylmalonic ester instead of methylmalonic ester. The isopropyl group has been shown[6] to be effective in blocking certain alkylations. With this group present, the alkylation amounted to only 45% of the theoretical at 140–160°, but no trace of any condensation product could be isolated from the reaction.

Just as methylmalonic ester failed to undergo an acetoacetic ester condensation with itself, it also failed to condense with ethyl isobutyrate. This intermolecular condensation would be expected from the similarity in structure between these esters (IV) and ethyl α-ethyl-α′-carbethoxyadipate (V) which has been shown[7] to undergo intramolecular condensation with the formation of 2-ethyl-2,5-dicarbethoxycyclopentanone.

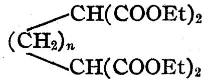

IV

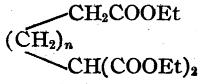

V

These esters (IV) failed to enter into any intermolecular condensation. The only product, besides the starting materials, which was isolated from the reaction was a small amount of monoethyl methylmalonate.

On the basis of our present knowledge no reasonable explanation is available to account for the ready intramolecular condensation of such esters as I and V and the failure of such esters as III and IV to undergo an intermolecular condensation. This failure, however, by emphasizing the necessity of a structure that permits an intramolecular condensation, suggested the investigation of the behavior of some other methylene dimalonic esters, the intramolecular condensation of which would yield cyclic products containing cycles other than those of conventional five or six members.

In this connection methylene dimalonic ester (VI, $n = 1$), pentamethylene dimalonic ester (VI, $n = 5$) and decamethylene dimalonic ester (VI, $n = 10$) were investigated. These esters, if they condensed intramolecularly in the manner of I, would yield products containing four, eight and thirteen membered rings, respectively.


VI


VII

None of these dimalonic esters gave any evidence of intramolecular condensation when heated with sodium ethoxide. Methylene dimalonic ester yielded ethyl acrylate, malonic ester, ethyl α-carbethoxyglutarate (VII, $n = 1$) and a relatively large amount of an undistillable tar. The first two of the products are probably the result of a retrograde Michael reaction on VII ($n = 1$). The best explanation for the unusually large amount of tar is from the polymerization of methylene malonic ester which, along with malonic ester, would result from a retrograde Michael reaction on the starting ester (VI, $n = 1$). Pentamethylene dimalonic ester yielded only de-carboxylated products, ethyl azelate and ethyl α-carbethoxyazelate (VII, $n = 5$). Decamethylene dimalonic ester yielded no product boiling lower than itself. The reaction product was a viscous liquid which could not be distilled and appeared to be an intermolecular condensation product.

Experimental

Methylmalonic ester was prepared by the Wislicenus[8] procedure, in yields of 60–70% of the theoretical. The product obtained boiled at 194–196°.

Reaction of Methylmalonic Ester with Sodium Ethoxide.—One mole (174 g.) of methylmalonic ester was heated with 0.5 mole of sodium ethoxide at 160° for eight hours. The apparatus was arranged so that any distillate could be collected. The distillate on fractionation yielded the following fractions: (a) alcohol, b. p. 75–78°, 25.8 g.; (b) ethyl propionate, b. p. 98–104°, 7.0 g.; (c) ethyl α-

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(5) *Cf.* Michael, *J. prakt. Chem.*, [2] **72**, 547, 550 (1905).

(6) Preiswerk, *Helv. Chim. Acta*, **6**, 192 (1923).

(7) Meincke and McElvain, THIS JOURNAL, **57**, 1443 (1935).

(8) Wislicenus, *Ann.*, **246**, 315 (1888); *Ber.*, **27**, 796 (1894).

methylbutyrate, b. p. 125–132°, sap. equiv. 129 (calcd. 130), 2.2 g.

The reaction mixture, after cooling, was treated with a cold solution of 35% sulfuric acid, the precipitated $Na_2SO_4 \cdot 10H_2O$ filtered off, and the filtrate fractionated. The following fractions were collected from this filtrate: (d) ethyl propionate, b. p. 98–100°, 4 g.; (e) ethyl α-methylbutyrate, b. p., 130–131°, 10.7 g.; (f) methylmalonic ester, b. p. 194–196°, 53.4 g.; (g) ethyl methylethylmalonate, b. p. 205–208°, sap. equiv., 102 (calcd. 101), 57.0 g.; (h) monoethyl methylmalonate, b. p. 100–102° (2 mm.), 13.0 g., sap. equiv. 71 (calcd. 73), n^{25}_{D} 1.4235, d^{25}_{25} 1.1192.[9] Analyses calcd. for $C_6H_{10}O_4$: C, 49.3, H, 6.85; OC_2H_5, 30.8. Found: 49.4, 6.84, 30.2.

The total quantity of alkylated products, methylethylmalonic ester and α-methylbutyric ester from the above run amounted to 72.1% of the theoretical.

When methylmalonic ester was allowed to react with sodium ethoxide at 50–60° and also at 120° for six hours and the product worked up in the same manner as described above, the only product which was isolated was the mono-ethyl methylmalonate. If, however, dry hydrogen chloride instead of 35% sulfuric acid was used to decompose the reaction mixture, unchanged methylmalonic ester was the only product recovered.

Isopropylmalonic Ester.—This ester was prepared in 56% yield by alkylation of sodiomalonic ester suspended in alcohol with isopropyl bromide. The product, washed free of unreacted malonic ester with 25% potassium hydroxide, boiled 211–212°.[10]

Reaction of Isopropyl Malonic Ester with Sodium Ethoxide.—One-half mole (101 g.) of isopropylmalonic ester was allowed to react with 0.25 mole of sodium ethoxide for eighteen hours at 150–160°. During this time 8.5 g. of alcohol distilled from the reaction mixture. When the reaction mixture was worked up as described above, the following fractions were collected: (a) ethyl isovalerate, b. p. 132–134°, sap. equiv. 133 (calcd. 130), 11.0 g.; (b) ethyl α-isopropylbutyrate, b. p. 158–162°, 4.7 g., derived acid, b. p. 203°,[11] neut. equiv. 130 (calcd. 130); (c) isopropylmalonic ester, b. p. 91–92° (8 mm.), 29.8 g.; (d) ethylisopropylmalonic ester, b. p. 81–82° (2 mm.), 15.5 g., derived acid, m. p. 132–133°;[11] (e) b. p., 100–110° (2 mm.), 5.0 g.

Fraction e was heated to 140° in order to decarboxylate any mono-ethyl ester. Only 75 cc. of carbon dioxide was obtained from a 4-g. sample, the theoretical amount being 560 cc., had the sample been pure half ester. This amount of carbon dioxide corresponds to 0.67 g. of half ester. The remainder boiled 134–136° (10 mm.) and was found to be identical with ethylisopropylmalonic ester (fraction d).

The alkylated products, fractions b, d, and e, are equivalent to 23.4 g. of starting material and represent a yield of 45% of the theoretical.

Attempted Condensation of Ethyl Isobutyrate with Methylmalonic Ester.—To one-half mole of sodium ethoxide was added one mole (174 g.) of methylmalonic ester. (The alcohol formed was removed at 50° under diminished pressure.) To this was added two moles (232 g.) of ethyl isobutyrate and the mixture refluxed for ten hours. The amounts of the various products isolated were: 195 g. of ethyl isobutyrate (107–110°); 126 g. of methylmalonic ester (194–196°); 7 g. of monoethyl methylmalonate [100–110° (2 mm.)].

Reaction of Methylene Dimalonic Ester with Sodium Ethoxide.—A mixture of one-half mole of sodium ethoxide and one-half mole (166 g.) methylene dimalonic ester, prepared according to Welch,[12] was heated at 110–115° for eight hours. During this period of heating 11.6 g. of alcohol distilled out. The pressure was then reduced to 400 mm. and 2.8 g. of ethyl carbonate distilled over. The reaction mixture was decomposed with 35% sulfuric acid, cooled, and the $Na_2SO_4 \cdot 10H_2O$ filtered off. Fractionation of the filtrate yielded (a) 21.2 g. of a fraction, b. p. 80–110°, composed of a mixture of alcohol and ethyl acrylate which from saponification values contained 7.6 g. of ethyl acrylate; (b) 12.2 g. of malonic ester, b. p. 195–198°; (c) 13.2 g. α-carbethoxyglutaric ester, b. p. 149–151° (7 mm.);[13] (d) 15.2 g. of starting ester, methylene dimalonic ester, b. p. 150–153° (2 mm.). The undistilled residue from this run amounted to 78 g.

Preparation of Pentamethylene Dimalonic Ester.—This was prepared according to the method of Perkin[14] except that the sodiomalonic ester was prepared in benzene. The ester, boiling 194–199° (1 mm.), was obtained in 24% yield.

Reaction of Pentamethylene Dimalonic Ester with Sodium Ethoxide.—Sixty two grams (0.14 mole) of pentamethylene dimalonic ester was heated with 0.08 mole of sodium ethoxide at 120–130° for eight hours. During this time 2.2 g. of alcohol distilled from the reaction. The reaction mixture was treated with 35% sulfuric acid and after filtering off the $Na_2SO_4 \cdot 10H_2O$ the filtrate fractionated. Fraction (a) 5 g., b. p. 115–125°, was ethyl azelate; sap. equiv. 131 (calcd. 122), m. p. of derived azelaic acid 105–106° and its *p*-phenylphenacyl ester 145–146°;[15] fraction (b) 10 g., b. p., 125–150°; fraction (c) 17.8 g., b. p. 150–165°; fraction (d) 12.2 g., b. p. 165–170°.

The acids derived from (d) were decarboxylated to determine the amount of α-carboxyazelaic acid, a compound which has not been described previously. The carbon dioxide obtained when the acids from (d) were heated indicated that the mixed acids from (d) contained 67% α-carboxyazelaic acid. The acid remaining after the evolution of the carbon dioxide was azelaic acid.

Considerable evolution of carbon dioxide was observed during the isolation of the acids from fractions (b) and (c). This indicates that these fractions were also mixtures of ethyl azelate and ethyl α-carbethoxyazelate.

Decamethylene dimalonic ester was prepared by reaction of decamethylene bromide with a benzene suspension of sodiomalonic ester.[16] All material boiling below 160° (0.2 mm.) was removed. The residue, which could not be readily distilled, amounted to 36% of the theoretical yield.

Reaction of Decamethylene Dimalonic Ester with Sodium Ethoxide.—Two hundred twenty-nine grams of the residue obtained above was heated with one-half mole

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[9] *Cf.* Marguery, *Bull. soc. chim.*, [3] **33**, 542 (1905).

[10] Conrad and Bischoff, *Ann.*, **204**, 144 (1880).

[11] Crossley and LeSueur, *J. Chem. Soc.*, **77**, 92 (1900).

[12] Welch, *ibid.*, 673 (1931).

[13] Emery, *Ber.*, **24**, 282 (1891).

[14] Perkin, *J. Chem. Soc.*, **65**, 92 (1894).

[15] Drake and Sweeney, This Journal, **54**, 2059 (1932).

[16] Franke and Hankam, *Monatsh.*, **31**, 177 (1910).

of sodium ethoxide at 130° for six hours. During this time, only 3.2 g. of alcohol distilled from the reaction. On working up the reaction mixture in the manner described for the other dimalonic esters nothing could be distilled from the reaction product even at 230° and under 0.4 mm. pressure. This product, which was much more viscous than the starting material, was probably an intermolecular condensation product, and was not investigated further.

Summary

A study of the behavior of methylmalonic ester, isopropylmalonic ester, methylene dimalonic ester, pentamethylene dimalonic ester and decamethylene dimalonic ester with sodium ethoxide has been made. The main reaction product in the cases of the monosubstituted malonic esters was the dialkylmalonic ester resulting from self-alkylation of the starting esters. There was no evidence of an intermolecular condensation product in either case.

With the methylene dimalonic esters no intramolecular condensation could be effected. When the reaction products could be identified they were found to be decomposition products, resulting from retrograde Michael reactions and decarboxylation, of the starting esters.

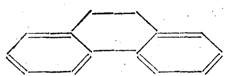
MADISON, WISCONSIN RECEIVED OCTOBER 20, 1936

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydrogenation of Phenanthrene

BY JOHN R. DURLAND AND HOMER ADKINS

Three substances, 9,10-dihydrophenanthrene[1,3] (I), 1,2,3,4,5,6,7,8-octahydrophenanthrene[2,3,4] (II), and tetradecahydrophenanthrene[5] (III), have been made by the catalytic hydrogenation of phenanthrene. Incidental to an investigation of the relation of structure to the hydrogenation of certain phenanthrene derivatives we have developed procedures for the preparation of these compounds which may be of immediate value to others.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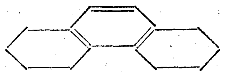
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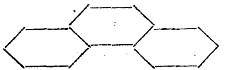
III

Burger and Mosettig took advantage of the greater activity of copper–chromium oxide[6] toward olefinic double bonds as compared with benzenoid nuclei[7] and selectively hydrogenated phenanthrene at 220°, obtaining 9,10-dihydrophenanthrene in yields of about 80%. We have duplicated their results. However, with a purer sample of phenanthrene we have obtained no dihydrophenanthrene at 220°. With this purer sample of phenanthrene we have been able to hydrogenate in the 9,10-position with copper–chromium oxide at 130° within four hours, as compared with the eight to ten hours at 220° reported by Burger and Mosettig. The best temperature for the production of 9,10-dihydrophenanthrene with copper–chromium oxide appears to be about 150°, the yield being 87%. At 180° a little octahydrophenanthrene was produced, while at 220° the latter is produced to the exclusion of the dihydro compound.

The fact that phenanthrene may be hydrogenated in the 9,10-position over copper–chromium oxide at 130° is rather striking evidence of the olefinic character of the double bond in that position. Copper–chromium oxide is not usually active toward any type of unsaturation at temperatures much below 130°.

With pure phenanthrene, Raney nickel may also be used for the preparation of dihydrophenanthrene. When the reaction was carried out at 96°, a 61% yield was obtained after five hours. However, nickel is not so satisfactory as copper–chromium oxide for this selective hydrogenation. With copper–chromium oxide there is a difference of about 50° between the temperature at which hydrogenation begins in the 9,10-position and the temperature required for further hydrogenation. With Raney nickel the temperature differential for these two types of reaction is no more than 10°. These facts are indicated by a com-

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(1) Burger and Mosettig, THIS JOURNAL, **57**, 2731 (1935); **58**, 1857 (1936).

(2) Van de Kamp and Mosettig, *ibid.*, **57**, 1107 (1935).

(3) Schroeter, *Ber.*, **57**, 2025 (1924); Schroeter, Müller and Huang, *ibid.*, **62**, 645 (1929).

(4) Ipatieff, *ibid.*, **41**, 999 (1908).

(5) Pinkney and Marvel, THIS JOURNAL, **58**, 976 (1936).

(6) Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

(7) Adkins and Connor, *ibid.*, **53**, 1091 (1931).

parison of the data for experiments 1 and 5 (Ni) and 2, 4 and 8 (CuCrO).

Either Raney nickel or copper–chromium oxide may be used for the preparation of octa- or tetradecahydrophenanthrene, but nickel is to be preferred. Octahydrophenanthrene is best made at 120°, the time for pure phenanthrene with Raney nickel being only four or five hours instead of two to eight days at 120 to 140° as with less pure material.[2] Tetradecahydrophenanthrene is best made at about 200° with Raney nickel, the time required being three or four hours.

The copper–chromium oxide catalyst usually has been found to be inactive toward phenyl groups. However, as Folkers has pointed out,[8] this inactivity is merely relative and under certain drastic conditions even phenyl groups may be hydrogenated. In this Laboratory cyclohexyl derivatives have been produced over copper–chromium oxide from ethyl salcylate,[9] N-substituted phthalimides[10] and N-phenyl pyrrole.[11] The conversion of 9,10-dihydrophenanthrene to 1,2,3,4,5,6,7,8-octahydrophenanthrene is not a clear cut indication of the activity of copper–chromium oxide for the hydrogenation of a benzoid nucleus since this transformation apparently involves intramolecular rearrangement. However, the conversion of the octahydrophenanthrene to tetradecahydrophenanthrene at 300° is fairly clear evidence for the activity of copper–chromium oxide in catalyzing the hydrogenation of a benzenoid nucleus in a hydrocarbon.

Experimental Part

Crude phenanthrene was purified by a combination and modification of the procedures used by Bachmann[12] and by Schroeter.[3] The former used an oxidizing agent but no sodium, the latter sodium but no oxidizing agent. One kilogram of "70% phenanthrene" (Eastman) was heated with six liters of 95% alcohol and the hot solution decanted from the insoluble portion (discarded) and cooled. The crystallized phenanthrene was dissolved in 2400 ml. of glacial acetic acid. To the boiling solution was added gradually a solution of 100 g. of sodium dichromate dihydrate in 20 ml. of sulfuric acid and 150 ml. of 50% acetic acid. Thirty ml. of sulfuric acid was then added slowly and the solution refluxed for fifteen minutes. After pouring the hot solution into an equal volume of cracked ice and water, the mixture was filtered and the phenanthrene washed with water until a colorless filtrate was obtained. After drying at 80° the product was fractionated carefully through a Widmer column, b. p. 181–183° (15 mm.). (The yield but not the purity of the final product was increased about 20 g. by one crystallization of this distillate from ethyl alcohol.) The distillate was heated for four hours at 200° with 10% of its weight of metallic sodium, the mixture being *stirred vigorously during the entire period.* The phenanthrene was distilled with care in a Claisen flask with a thin plug of glass wool in the side neck. The colorless product was fractionated over 5 to 10 g. of metallic sodium through a Widmer column, the low boiling fractions (diphenyl) being discarded. The pure product weighed 480–530 g., melted at 97–98°, and was perfectly colorless even in the liquid state. An additional 70–80 g. of impure phenanthrene was recovered by subliming all residues from the sodium treatment.

The reaction mixtures after hydrogenation were fractionated through a Widmer column having a glass spiral 15 cm. in length. The fractions considered to be dihydrophenanthrene were taken at 176–178° (20 mm.) or 140–142° (6 mm.). The octahydrophenanthrene fractions were taken at 172–173° (20 mm.) or 135–136° (6 mm.). Tetradecahydrophenanthrene was taken at 147–149° (20 mm.) or 142–144° (15 mm.). The best indication of the purity of the hydrogenated phenanthrenes so obtained is given by a comparison of the refractive indices of the products as given in Table I with those of more thoroughly purified products, and with those previously reported. Dihydrophenanthrene after one crystallization from methanol melted 33.8 to 34.4° and the supercooled material showed a $n^{25}\mathrm{D}$ of 1.6406. Octahydrophenanthrene was purified through the sulfonic acid as described by Schroeter. The pure compound so obtained, b. p. 134–135° (5 mm.), m. p. 16.6°, showed a $n^{25}\mathrm{D}$ of 1.5640, a figure almost identical with that of material purified only by a careful frac-

TABLE I

HYDROGENATION OF PHENANTHRENE

Reaction in a steel vessel under 150 to 200 atm. pressure of hydrogen in (a) 50 ml. methylcyclohexane or (b) 100 ml. ethanol as a solvent. (c) 32% and (d) 9% phenanthrene recovered. (c) 2% yield of octahydrophenanthrene. (f) 28 to 31% yield of a mixture having a refractive index averaging about 1.54. (g) 11% yield of octahydrophenanthrene.

	$C_{14}H_{10}$, g.	Catalyst, g.	°C.	Hrs.	% yield	$n^{25}\mathrm{D}$
			9,10-Dihydrophenanthrene			
1	50(a)	5 Ni	96	5.0	61(c)	1.6295
2	40(b)	4CuCrO	130	4.0	79(d)	1.6343
3	40(b)	4 CuCrO	150	3.0	87	1.6334
4	40(b)	4 CuCrO	180	1.5	88(e)	1.6253
			1,2,3,4,5,6,7,8-Octahydrophenanthrene			
5	50(a)	5 Ni	110	5.2	79	1.5640
6	50(a)	10 Ni	120	4.0	94	1.5611
7	100(a)	5 Ni	120	5.0	82	1.5630
8	40(b)	4 CuCrO	200	11.0	63(f)	1.5650
9	40(b)	4 CuCrO	220	6.0	64(f)	1.5631
			Tetradecahydrophenanthrene			
10	40(a)	5 Ni	(150–200)	9.0	89	1.5050
11	20(a)	3 Ni	200	3.1	82	1.5050
12	30(a)	3 CuCrO	300	9.0	50(f) (g)	1.5035

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[8] Folkers, THIS JOURNAL, **58**, 1559 (1936).

[9] Connor and Adkins, *ibid.*, **54**, 4658 (1932).

[10] Wojcik and Adkins, *ibid.*, **56**, 2419 (1934).

[11] Signaigo and Adkins, *ibid.*, **58**, 709 (1936).

[12] Bachmann, *ibid.*, **57**, 555 (1935).

tionation. Rehydrogenation and refractionation of the tetradecahydrophenanthrene gave a product, b. p. 155–157° (27 mm.), having $n^{25}D$ of 1.5003 which agrees with the value given by Pinkney and Marvel.[5]

In the fractionation of the reaction mixtures there were intermediate fractions which are not reported in the table. Their amounts in most cases represented only a few per cent. of the weight of phenanthrene originally used. However, with copper–chromium oxide at temperatures of 200–300° these unidentified products amounted to about 30% of the weight of phenanthrene submitted to hydrogenation.

Summary

Methods have been given for the preparation of 9,10-dihydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene, and tetradecahydrophenanthrene from "70% phenanthrene."

MADISON, WIS. RECEIVED NOVEMBER 23, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Molecular Rearrangements in the Sterols. I. The Action of Anhydrous Potassium Acetate on Cholesteryl *p*-Toluenesulfonate in Acetic Anhydride Solution

BY EVERETT S. WALLIS, E. FERNHOLZ AND F. T. GEPHART

The epimerization of the hydroxyl group of cholesterol and other unsaturated sterols has become of great interest since Ruzicka[1] showed that the male hormone, androsterone, is a derivative of *epi*-dihydrocholesterol, and that its physiological activity is much greater than the corresponding epimer.

This difference in the activity of the two isomers stimulated our interest in the preparation of the epimer of dehydroandrosterone. In order to find a satisfactory method for the preparation of this latter compound we first thought it advisable to study possible methods for the epimerization of cholesterol, since the previous attempts of Stoll[2] to prepare *epi*-cholesterol had failed.

During the course of this investigation three papers have appeared which have an important bearing on this problem. Evans and Schoenheimer[3] have reported the preparation of *epi*-allocholesterol, which differs from *epi*-cholesterol only in the position of the double bond. Marker, Oakwood and Crooks[4] have described the preparation of *epi*-cholesterol by the action of oxygen on the Grignard reagent obtained from cholesteryl chloride. Beynon, Heilbron and Spring[5] have published experimental results obtained in an investigation of some reactions of the isomeric ethers of cholesterol.

These publications make it advisable to report certain experiments we have carried out on the problem of obtaining *epi*-cholesterol in good yields, and which also have interest regarding the constitution of the two series of isomeric ethers of cholesterol, discovered by Stoll.[2]

Stoll[2] found that when cholesteryl *p*-toluene sulfonate is boiled with an alcohol it reacts easily to form a normal levorotatory ether, but that an isomeric dextrorotatory ether is formed when the reaction is carried out in the presence of potassium acetate. Stoll[2] expressed the opinion that this new ether was a derivative of *epi*-cholesterol or of *epi*-allocholesterol.

In the same year Wagner-Jauregg and Werner[6] reported that cholesteryl chloride and bromide behaved in a similar manner, that is, when heated alone with alcohols the normal levorotatory ether is formed, but in the presence of potassium acetate the isomeric dextrorotatory ether is produced. They further observed that the isomeric methyl ether is converted into the normal ether when heated with hydrogen chloride in methyl alcohol at 130°. From this fact they concluded that in the formation of ethers from either cholesteryl halides or the *p*-toluene sulfonate the isomeric ethers are first formed, but that the acid produced in the reaction converts them into the so-called "normal" form. These investigators also attempted to hydrogenate the isomeric ether. Although they found that this reaction did not proceed smoothly, it is important to note in view of certain of our experiments about to be described that a small amount of the normal dihydrocholesteryl methyl ether was isolated.

In this connection the observations of Beynon, Heilbron and Spring[5] are also of special interest.

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[1] Ruzicka and co-workers, *Helv. Chim. Acta*, **17**, 1395 (1934).

[2] Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

[3] Evans and Schoenheimer, THIS JOURNAL, **58**, 182 (1936).

[4] Marker, Oakwood and Crooks, *ibid.*, **58**, 481 (1936); see also, Marker, Kamm, Oakwood and Laucius, *ibid.*, **58**, 1948 (1936).

[5] Beynon, Heilbron and Spring, *J. Chem. Soc.*, 907 (1936).

[6] Wagner-Jauregg and Werner, *J. physiol. Chem.*, **213**, 119 (1932).

These authors made a study of the hydrolysis of the two series of cholesteryl ethers with the idea in mind that the "abnormal" ethers might be derivatives of *epi*-cholesterol. They found that whereas the normal ethers are not hydrolyzed by halogen acids in acetic acid solution the isomeric ethers react quite readily with halogen acids to produce the normal cholesteryl halides. They also observed that by the action of bromine the alkoxyl group in the isomeric ethers is replaced by bromine. In each case studied 3,5,6-tribromocholestane was produced. The normal ethers reacted normally to give a stable dibromide.

In this paper we wish to report certain experimental results obtained by us in a search for a satisfactory method for the preparation in good yields of the epimeric modifications of certain unsaturated sterols. Our method of attack was also based upon certain experiments of Phillips[7] carried out on alcohols containing only one asymmetric carbon atom, and it involved an investigation of the action of potassium acetate on cholesteryl *p*-toluene sulfonate. But in order to avoid the complication of the formation of ethers, and since we had observed that in acetic acid solution the normal cholesteryl acetate is formed, the reaction was carried out with anhydrous potassium acetate in acetic anhydride solution. This indeed yielded a new acetate, isomeric with cholesteryl acetate, which at first we were inclined to believe was *epi*-cholesteryl acetate. Experiments soon showed, however, that this was not the case.

This new acetate which we shall now call *i*-cholesteryl acetate is *strongly dextrorotatory*, $[\alpha]^{20}\text{D}$ +47.8°, and melts at 73°. Hydrolysis yields *i*-cholesterol. This compound crystallizes from alcohol in long needles which melt at room temperature. The substance resolidifies and passes into another crystalline form which melts at 74–75°. *i*-Cholesterol is strongly *dextrorotatory*, $[\alpha]^{20}\text{D}$ +23.9°. It is not precipitated by digitonin. Reacetylation yields the above *i*-cholesteryl acetate.

Experimental results obtained in a study of the catalytic hydrogenation of this new acetate are of special interest. Palladium black was found to be entirely ineffective in bringing about the hydrogenation. Platinum black brought about a very slow reaction. On working up the products there was isolated, besides the starting material, some cholestane. The Adams platinum oxide catalyst produced an entirely different result. When the platinum oxide was reduced in presence of the *i*-cholesteryl acetate a rapid hydrogenation took place and dihydrocholesteryl acetate was formed in good yield. This fact strongly indicates that an inversion of the hydroxyl group does not occur during the formation of *i*-cholesterol. It also suggests a close relationship to the "abnormal" ethers discussed above since, as has already been pointed out, Wagner-Jauregg and Werner[6] isolated dihydrocholesteryl methyl ether from the hydrogenation products of the "abnormal" ether.

There are other important facts which should be recorded. *i*-Cholesteryl acetate does not react with perbenzoic acid. Neither does it decolorize readily a solution of bromine in carbon tetrachloride. The Liebermann reaction, however, is quite strong. This inertness toward bromine and perbenzoic acid, and the relatively great stability toward catalytic hydrogenation, suggest that a double bond as such is not present in *i*-cholesteryl acetate and *i*-cholesterol.

Experiments were carried out to determine the nature of the hydroxyl group in *i*-cholesterol. It was found that *i*-cholesterol could be oxidized easily with chromic acid in acetic acid solution. From the products formed we were able to isolate an oxime in a 20% yield. This leads to the conclusion that *i*-cholesterol is a secondary alcohol.

In certain reactions a conversion of *i*-cholesterol to cholesterol was observed. For example, in the course of the preparation of the 3,5-dinitrobenzoate of *i*-cholesterol the interesting observation was made that when the reaction was carried out by heating the mixture of pyridine, dinitrobenzoyl chloride and *i*-cholesterol for one hour on the water-bath it was possible to isolate in a yield of 18% the normal cholesteryl dinitrobenzoate (m. p. 193° $[\alpha]^{18}\text{D}$ −14.6°). If, however, the reaction was carried out at room temperature only small amounts of the normal cholesteryl dinitrobenzoate were produced. In another experiment *i*-cholesteryl acetate was dissolved in acetic acid, and after the addition of two drops of sulfuric acid the mixture was heated on the water-bath for one hour. Partial conversion to cholesteryl acetate took place, and hydrolysis gave a product precipitable with digitonin.

All these facts lead to the conclusion that the reaction of anhydrous potassium acetate on

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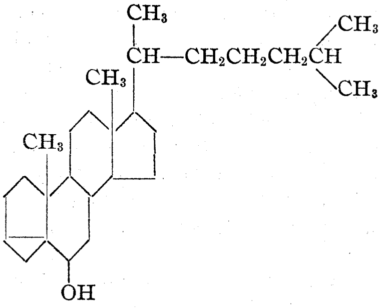
[7] Phillips, *J. Chem. Soc.*, **123**, 44 (1925). Other papers by Phillips and co-workers have appeared since this time.

cholesteryl *p*-toluene sulfonate in acetic anhydride solution is accompanied by a molecular rearrangement. The exact nature of this rearrangement is still obscure. At the present time, however, we believe that in *i*-cholesterol and its derivatives the carbon skeleton is different, and that the reaction may involve a type of rearrangement common in certain terpenes, but until now unknown in sterol chemistry. Such a rearrangement would produce a compound whose structure could be represented in the following manner.



This type of formulation would explain the apparent non-reactivity of the double bond, since it is not present as such in the molecule. The assumed structure represents the molecule as a secondary alcohol, and therefore explains the formation of a ketone on oxidation with chromic acid. It also accounts for the conversion of *i*-cholesterol and its acetate under suitable conditions into cholesterol and its derivatives.

In conclusion we wish to state that regardless of the true nature of the structure of *i*-cholesterol, the experimental facts above described strongly suggest that a close relationship exists between this new compound and the so-called "abnormal" ethers of Stoll. This relationship is being investigated further.

Experimental Part

Preparation of Cholesteryl *p*-Toluene Sulfonate.—This compound was prepared by the method of Freudenberg[8] with the following modifications. After dissolving by gentle warming 58.2 g. of dried cholesterol in 70 cc. of dried pyridine, 58.2 g. of *p*-toluenesulfonyl chloride was added. Within five minutes a white crystalline precipitate began to form. After the mixture had stood overnight, the product was taken up in ether, worked up in the usual manner, and finally recrystallized from dry ether; yield, 72.1 g. (89.3%); m. p. 131.5–132.5°.

Preparation of *i*-Cholesteryl Acetate.—One hundred grams of anhydrous potassium acetate was dissolved in 1500 cc. of boiling acetic anhydride (pure). The solution was cooled to 50° whereupon potassium acetate crystallized in a finely divided state. To this mixture was added 35 g. of cholesteryl *p*-toluenesulfonate. The flask was then placed on the steam-bath, and stirred for approximately thirty-six hours. During this time the temperature inside the flask varied from 70–80°. The dark brown mixture was poured into cold water; 800 cc. of ether was added and the ether layer was washed repeatedly with a cold aqueous solution of potassium carbonate. (In a later experiment the acetic anhydride was removed by distillation under diminished pressure.) After complete removal of the acetic anhydride and acetic acid the ether layer was dried with anhydrous sodium sulfate, decolorized with animal charcoal and the ether removed by distillation. An oily product was obtained. This material was dissolved in alcohol, and small amounts of ether were added. Crystallization was carried out in such a manner as to obtain four crops of crystals: 3.6 g., m. p. 71.5°; 0.5 g., m. p. 70–71°; 4.7 g., m. p. 64–66°; 7.2 g., m. p. 59–62°. Several recrystallizations of the third and fourth fractions gave 0.4 g. of material, m. p. 71°, and 7.5 g., m. p. 67–68°. The combined weight of fractions of m. p. 68–71.5° was 12.0 g. (43.2%). The other products of the reaction consisted mainly of an unsaturated hydrocarbon and cholesteryl acetate.

It was found to be impossible to free the *i*-cholesteryl acetate from cholesteryl acetate by the process of recrystallization. Therefore, 7.5 g. of the above acetate of m. p. 67–68° was dissolved in 100 cc. of alcohol, and treated with 8 g. of potassium hydroxide. The solution was refluxed for one-half hour on the water-bath, poured into water and the product extracted with ether. The dried ether solution was evaporated to dryness and taken up in a small amount of 90% alcohol. A solution of 6 g. of digitonin in 500 cc. of 90% alcohol was then added. The mixture was cooled to room temperature and the digitonide was filtered and dried; weight 4.8 g. (corresponding to 1.2 g. of cholesterol).

The filtrate was evaporated to dryness, the residue was digested with ether, and, after removing the solvent, it was crystallized from alcohol. After thorough cooling in an ice–salt mixture the *i*-cholesterol which separated was collected rapidly, and placed in a vacuum desiccator where it melted and resolidified. The product weighed 3.5 g. and melted constantly at 74–75°, $[\alpha]^{20}_D$ +23.9° (22.6 mg. dissolved in 2 cc. of chloroform solution gave an α_D +0.27°, 100-mm. tube).

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.85; H, 11.92. Found. C, 83.75; H, 11.87.

The acetate was prepared by heating 1.5 g. of *i*-cholesterol with 10 cc. of acetic anhydride for one hour on the water-bath. The crystalline product which separated on cooling was recrystallized from alcohol; yield 1.4 g., m. p. 73°, $[\alpha]^{20}_D$ +47.8° (25.1 mg. in 2 cc. chloroform solution gave α_D +0.60).

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.23; H, 11.29. Found: C, 81.32; H, 11.39.

Catalytic Hydrogenation of *i*-Cholesteryl Acetate.—(a) After reducing 1.07 g. of platinum oxide suspended in 50 cc. of acetic acid with hydrogen, 1 g. of *i*-cholesteryl acetate was added. Hydrogen was absorbed slowly and after five hours the reaction was stopped. After removal of the solvent the material was crystallized from alcohol. This

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[8] Freudenberg and Hess, *Ann.*, **448**, 128 (1926).

gave 0.29 g. of starting material, m. p. 70°. The material remaining in the mother liquor was hydrolyzed with alcoholic potassium hydroxide and on crystallization from acetone there was obtained a substance, m. p. 78°, which did not depress the melting point of authentic cholestane; $[\alpha]^{20}_D$ +22.5° (22.2 mg. in 2 cc. chloroform solution gave $[\alpha]^{20}_D$ +0.25 1 dm. tube; lit. +24.7°).

(b) In a second experiment 1.332 g. of *i*-cholesteryl acetate was shaken with 1.30 g. of PtO_2 and 50 cc. of glacial acetic acid in an atmosphere of hydrogen, at room temperature, and at ordinary pressure. In fifteen minutes 310 cc. of hydrogen was absorbed. After hydrolysis with alcoholic potassium hydroxide, there was obtained a crystalline product which after thorough drying melted at 140°, and was identified by mixed melting point determination as dihydrocholesterol (cholestanol); yield, 1.1 g., or 85%.

Titration of *i*-Cholesteryl Acetate with Perbenzoic Acid.—Two samples of *i*-cholesteryl acetate were dissolved in chloroform, an excess of perbenzoic acid dissolved in the same solvent was added and the solutions were kept at 0°. Blanks were also run for comparison. Sample 1: 39.6 mg. consumed 0.079 mg. oxygen in forty-eight hours. Theoretical for 1 atom of oxygen 1.64 mg. oxygen. Sample 2: 56.0 mg. consumed 0.198 mg. oxygen in six days. Theoretical for 1 atom of oxygen 2.32 mg. of oxygen. It readily can be seen from these results that practically no reaction took place.

It was also observed that both *i*-cholesterol and *i*-cholesteryl acetate would not decolorize a dilute solution of bromine in carbon tetrachloride.

Oxidation with Chromic Acid.—To a solution of 0.93 g. of *i*-cholesterol in 30 cc. of specially purified acetic acid (potassium permanganate method), a solution of 0.64 g. of chromic acid in 20 cc. acetic acid was added drop by drop. The solution became temporarily cloudy and a slight rise in temperature was observed. After standing overnight at room temperature the mixture was extracted with ether. The ether was shaken with an aqueous solution of 2 *N* sodium hydroxide to remove the acidic material. Attempts to obtain a crystalline material from this acidic portion were unsuccessful. The neutral part crystallized but had an unsharp melting point; yield 0.33 g.

This crude ketone was boiled for two hours with 0.3 g. of hydroxylamine hydrochloride and 0.5 g. of sodium acetate in 30 cc. of ethyl alcohol. The product was precipitated with water. Recrystallizations from dilute alcohol gave small leaflets which when thoroughly dried melted at 143–144°; yield 0.2 g.

Anal. Calcd. for $C_{27}H_{45}NO$: C, 81.12; H, 11.35; N, 3.51. Found: C, 80.95; H, 11.58; N, 3.88.

Conversion of *i*-Cholesterol into Normal Cholesteryl *m*-Dinitrobenzoate.—A mixture of 0.574 g. of *i*-cholesterol (m. p. 74–75°), freed from cholesterol by means of digitonin, 0.6 g. of *m*-dinitrobenzoyl chloride, and 5 cc. of pyridine was heated for one hour in the water-bath. The material was taken up in ether and recrystallized from a mixture of acetone and alcohol; yield 0.16 g., m. p. 193°; $[\alpha]^{18}_D$ −14.5°. The product was identified by a mixed melting point determination as cholesteryl *m*-dinitrobenzoate.

Anal. Calcd. for $C_{34}H_{48}O_6N_2$: C, 70.30; H, 8.34. Found: C, 70.28; H, 8.37.

Conversion of *i*-Cholesteryl Acetate into Normal Cholesteryl Acetate.—After dissolving 0.1 g. of pure *i*-cholesteryl acetate (m. p. 73°) in 10 cc. of acetic acid, two drops of sulfuric acid were added, and the solution was heated on the water-bath for one hour. The solution was then worked up in the usual manner and a crystalline material was obtained which melted unsharply at 95–103°. Two recrystallizations from alcohol gave 0.03 g. of material which melted at 112–114° and showed no depression of the melting point when mixed with cholesteryl acetate (m. p. 114°).

Hydrolysis with alcoholic potassium hydroxide gave a product precipitable with digitonin.

We wish to take this opportunity to express our thanks to Merck & Company, Inc., Rahway, N. J., for all analyses published in this article, and for a grant-in-aid for this work.

Summary

The action of anhydrous potassium acetate on cholesteryl *p*-toluenesulfonate in acetic anhydride solution has been studied.

A new acetate and a new alcohol isomeric with cholesterol have been isolated. Certain properties of these two compounds, designated as *i*-cholesterol and *i*-cholesteryl acetate, have been described.

Evidence is submitted which leads to the conclusion that the reaction is accompanied by a molecular rearrangement.

It is further pointed out that the properties of this new alcohol suggest that a close relationship exists between it and the isomeric ethers of cholesterol discovered by Stoll.

PRINCETON, N. J. RECEIVED NOVEMBER 17, 1936

[FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE]

Oxidation–Reduction Potentials of β-Hydroxyphenazine and N-Methyl-β-oxyphenazine[1]

BY PAUL W. PREISLER AND LOUIS H. HEMPELMANN

The rapidly increasing number of type oxidation–reduction systems[2] shown to follow the mathematical formulations of the potentials of the two-step oxidation–reduction process[3] suggest that all electromotively active reversible oxidation–reduction systems are probably of this same general character. To gain further evidence on the important questions of the nature of the two-step process and of the effect on the potentials of the structure of the molecule and of substitution, a survey of the various types of systems is being conducted.

The potentials of β-hydroxyphenazine and of N-methyl-β-oxyphenazine (methyl aposafranone), because of their structural relation to the natural pigment pyocyanine, are of particular interest and are reported here. The oxidation–reduction reactions of β-hydroxyphenazine appear to involve both nitrogens of the phenazine nucleus, while those of N-methyl-β-oxyphenazine involve the oxygen and its para-position nitrogen. Both systems show clearly the two-step process in solutions more acid than *p*H 3 and a transformation into an apparent one-step process in solutions less acid. They illustrate the fundamental characteristics of their respective type systems and the effects of the ionizations of the components upon the oxidation–reduction potentials.

Experimental

β-Hydroxyphenazine was prepared[4] by condensing *o*-phenylenediamine and 2-hydroxy-1,4-quinone.[5] The resulting dark brown material was extracted repeatedly with boiling water and the extract was filtered off and allowed to cool slowly. The dark red hydrated crystals which were obtained were changed to the golden yellow anhydrous compound by heating to 110°.

N-Methyl-β-oxyphenazine was prepared by treating the acetyl derivative[4] of this yellow compound with methyl sulfate, decomposing the addition compounds so formed, and separating the desired material from isomeric substances. Recrystallization from water gave the characteristic dark red needle-like crystals.

The potentials of two platinum electrodes, immersed in the buffer containing the oxidant and its reduction products, were measured against a saturated calomel half-cell connected to the solution by a 5% agar-saturated potassium chloride bridge. Electrodes usually agreed to within 0.0002 volt and equilibrium conditions were attained rapidly. The calomel cell was standardized against a hydrogen electrode in 0.05 *M* potassium hydrogen phthalate. The *p*H values of the buffers were determined by a hydrogen electrode.

The substances used for buffers were: citrates from *p*H 1.48 to 4.73, phosphates from *p*H 5.79 to 6.71 and 10.69 to 11.69, carbonates from *p*H 9.13 to 9.54, and veronal from *p*H 7.48 to 8.52. Hydrochloric acid or sodium hydroxide was used to make up the more acid or more alkaline solutions.

The buffers were 0.05 to 0.10 *M* in buffering ion and the reactants about 0.0005 to 0.0001 *M*, as indicated. No corrections were made for the *p*H changes accompanying the reduction. An equivalent amount of sodium hydroxide was added to the titanous chloride titrating solutions to compensate for the excess of hydrochloric acid (7.493 *N*) in the commercial titanous chloride (1.29 *M*) preparations. Titanous chloride was used as reducing agent in buffers from *p*H 0.04 to 4.73 and sodium hydrosulfite in buffers less acid.

Commercial tank nitrogen, deoxygenated by passing over heated copper, was used to deoxygenate and stir the solutions. Temperature was maintained to within 0.1° of 30.0° by immersing the electrode vessels in a suitable bath.

The mixture of oxidant and its reduction products was made by titrating the deoxygenated, buffered oxidant solution with reducing agent similarly prepared. The solutions of N-methyl-β-oxyphenazine consisted of 50 cc. of buffer and 5 cc. of water containing 5 mg. of compound. The solutions of β-hydroxyphenazine consisted of 50 cc. of buffer, and 4 cc. of water and 1 cc. of an alcoholic solution containing 5 mg. for all buffers *p*H 0.04 to 1.48 and 8.40 to 9.54; 4.9 cc. water and 0.1 cc. for *p*H 2.05 to 5.79; and 4.8 cc. water and 0.2 cc. for *p*H 6.71 to 7.48. From 10 to 15 cc. of titrating solution was usually added.

Titrations of β-hydroxyphenazine by reducing agents, in buffers of higher *p*H than 9.54, and the alternative of reductions at lower *p*H and subsequent titrations at higher *p*H by oxidizing agents, did not give satisfactory results, probably because of the relatively high reducing intensity or the low solubility of the compounds.

The titration curves obtained for solutions at or below *p*H 2.05 show partial merging of the second step of the titrated system with the titanic–titanous system, however,

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(1) Presented before the American Society of Biological Chemists, Washington, D. C., March, 1936; Abstract, *J. Biol. Chem.*, **114,** lxxxi (1936).

(2) L. Michaelis, *Chem. Rev.*, **16,** 243 (1935); E. S. Hill and P. A. Shaffer, *J. Biol. Chem.*, **114,** li (1936); L. Michaelis, THIS JOURNAL, **58,** 873 (1936); P. W. Preisler and L. H. Hempelmann, *ibid.*, **58,** 2305 (1936).

(3) L. Michaelis, *J. Biol. Chem.*, **96,** 703 (1932); B. Elema, *Rec. trav. chim.*, **50,** 807, 1004 (1931); *J. Biol. Chem.*, **100,** 149 (1933).

(4) F. Kehrmann and F. Cherpillod, *Helv. Chim. Acta*, **7,** 973 (1924).

(5) R. Willstätter and F. Müller, *Ber.*, **44,** 2180 (1911).

by employing the proper geometrical method, a close estimation of the mid-point of the second step was attained.

The colors of the oxidants and the reductants in the hydrochloric acid solutions are various shades of yellow and the semiquinones are yellow-green. N-Methyl-β-oxyphenazine is red in solutions more alkaline than *p*H 5; a colorimetric determination of the ionization constant gave $pK = 3.05$, in close agreement with the electrometrically determined value of 3.0. Although the ionized forms of the oxidant and the reductant of β-hydroxyphenazine are deeper yellow than the un-ionized, the low solubility of the un-ionized forms prevent the accurate estimation of the ionization constants by visual methods.

Discussion

The characteristic points of the titration curves are given in the table and figures, $E'_{0\text{oxid-red}}$ being the mid-point or the 50% reduction point and $E'_{0\text{oxid-semi}}$ and $E'_{0\text{semi-red}}$ being the 25 and 75% reduction points of the curves of E'_0 against per cent. of reduction at the respective *p*H values. The quantities in parentheses were calculated[3] from the "index potentials," $(E_{1/4} - E_{3/4})/2$, and represent the mid-points of the separate one-equivalent curves, which in this region overlap or merge into each other.

POTENTIALS OF MIXTURES OF EQUIVALENT AMOUNTS OF OXIDANTS AND OF REDUCTANTS IN BUFFERS AT VARIOUS *p*H

	β-Hydroxyphenazine, volts				N-Methyl-β-oxyphenazine, volts			
*p*H	$E'_{0\text{oxid-red}}$	$\frac{E_{1/4} - E_{3/4}}{2}$	$E'_{0\text{oxid-semi}}$	$E'_{0\text{semi-red}}$	$E'_{0\text{oxid-red}}$	$\frac{E_{1/4} - E_{3/4}}{2}$	$E'_{0\text{oxid-semi}}$	$E'_{0\text{semi-red}}$
0.00			+0.297[a]	+0.079[a]			+0.316[a]	+0.078[a]
.04			.295	.077			.314	.076
.38			.274	.057			.295	.058
.78			.246	.033			.270	.042
1.09			.228	.020			.250	.036
1.48			.199	.007			.225	.029
2.05			.161	− .009			.187	.020
2.97	+0.027	+0.050	(+ .075	(− .021)	+0.070	+0.049	(+ .118)	(+ .022)
3.56	− .001	.030	(+ .020)	(− .022)	.039	.030	(+ .060)	(+ .018)
4.00	− .026	.022	(− .026)	(− .026)	.015	.022	(+ .015)	(+ .015)
4.46	− .053	.017	(− .081)	(− .025)				
4.73	− .069	.015			− .028	.017	(− .056)	(.000)
5.79	− .137	.014			− .092	.016	(− .127)	(− .057)
6.71	− .194	.014			− .151	.016	(− .186)	(− .116)
7.48	− .248	.014			− .193	.015		
8.40	− .316	.015						
8.52					− .225	.015		
9.13	−. 393	.014						
9.54	−. 436				− .314	.015		
10.69					− .361	.014		
11.69					− .397			
12.60					− .426	.015		

[a] Calculated.

By plotting the E'_0 values of the three systems against *p*H and projecting the straight line portions of the curves, intersections are formed which represent the ionization constants of the various species. Each essentially straight-line portion represents a region in which particular ionic or molecular species predominate and each intermediary curved portion represents a region of transition mixtures. The chemical reactions which probably predominate in these straight line portions reveal that the slope of any curve of E'_0 against *p*H is apparently determined by the number of hydrogen ions and electrons involved in the equilibria, being at 30° where $RT/F = 0.06$ volt

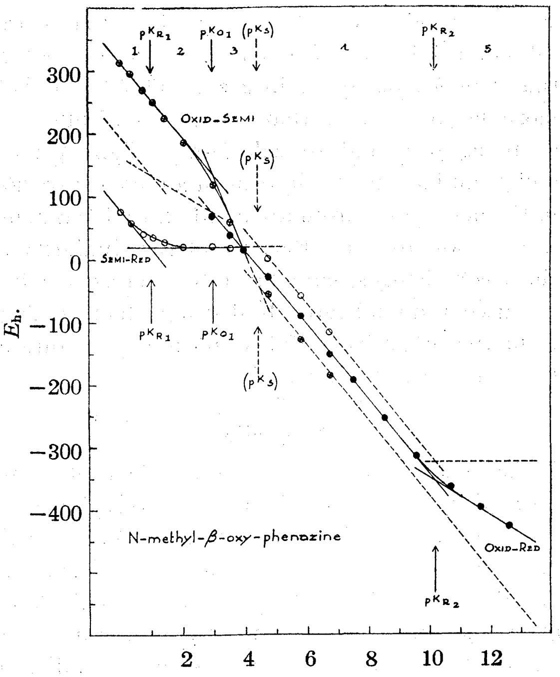
$$\frac{E'_0}{p\text{H}} = 0.06 \text{ volt} \times \frac{(\text{number of H}^+)}{(\text{number of electrons})}$$

The chemical equations for β-hydroxyphenazine for the sections as numbered at the top of Fig. 1, using "(pz)" to indicate the two phenylene nuclei connected by two nitrogen atoms without designating the positions of the double bonds or the unusual valencies or configurations of the semiquinone, are as follows:

The first equation of each pair represents the oxidant–semiquinone system and the second the semiquinone–reductant system: the sum of both would represent the oxidant–reductant system whose slope would be the mean value of the other two.

1. $\text{HO(pz)H}^+ + \text{e} + \text{H}^+ = \text{HO(pz)H}^+\cdot\text{H}$
(slope = 0.06 × 1/1 = 0.06)
$\text{HO(pz)H}^+\cdot\text{H} + \text{e} + \text{H}^+ = \text{HO(pz)H}^+\cdot\text{HH}$
(slope = 0.06 × 1/1 = 0.06)

2. $HO(pz)H^+ + e + H^+ = HO(pz)H^+ \cdot H$
(slope = 0.06 × 1/1 = 0.06)
$HO(pz)H^+ \cdot H + e = HO(pz) \cdot HH$
(slope = 0.06 × 0/1 = 0.00)
3. $HO(pz) + e + 2H^+ = HO(pz)H^+ \cdot H$
(slope = 0.06 × 2/1 = 0.12)
$HO(pz)H^+ \cdot H + e = HO(pz) \cdot HH$
(slope = 0.06 × 0/1 = 0.00)
4. $HO(pz) + e + H^+ = HO(pz) \cdot H$
(slope = 0.06 × 1/1 = 0.06)
$HO(pz) \cdot H + e + H^+ = HO(pz) \cdot HH$
(slope = 0.06 × 1/1 = 0.06)
5. $^-O(pz) + e + 2H^+ = HO(pz) \cdot H$
slope = 0.06 × 2/1 = 0.12)
$HO(pz) \cdot H + e + H^+ = HO(pz) \cdot HH$
(slope = 0.06 × 1/1 = 0.06)



pH.

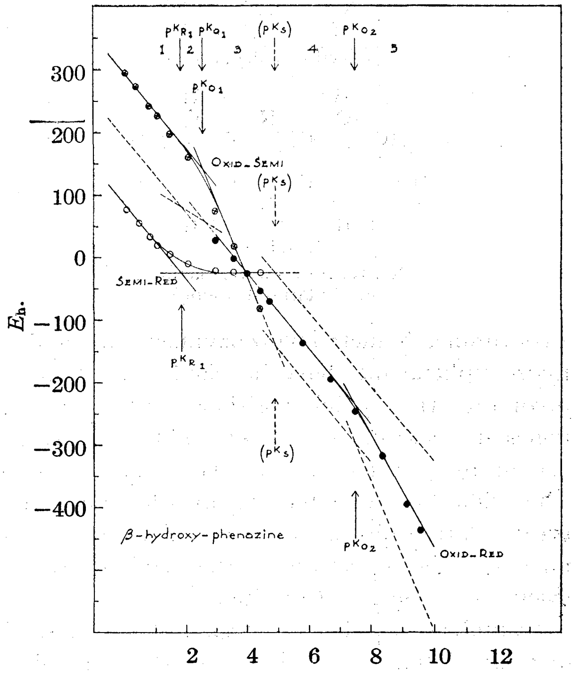
Fig. 1.

The ionization constants are: pK_{O_1} = 2.6 cation to free base; pK_{O_2} = 7.5, free base to anion; pK_S = (4.9) (approximate) cation to free base; pK_{R_1} = 1.8, cation to free base. The ionizations are accompanied by a noticeable change in color and an increase in solubility. The one additional anionic ionization in the semiquinone and the two in the reductant, which might occur at the hydrogens added in the reduction process, and the anionic ionization of the H from the OH group of the semiquinone and of the reductant are not evident in the pH regions studied.

The equations for N-methyl-β-oxyphenazine are of the same general character for the first four sections shown in Fig. 2, with the exception that the HO–group is replaced by an O= with consequent rearrangement of the double bonds and loss of one point of ionization, and the addition of a CH_3– group to the nitrogen atom meta to the oxygen. The equations for section 5 are

5. $(pzCH_3) + e + H^+ = (pzCH_3) \cdot H$
(slope = 0.06 × 1/1 = 0.06)
$(pzCH_3) \cdot H + e = (pzCH_3) \cdot {}^-H$
(slope = 0.06 × 0/1 = 0.00)

The ionization constants are: pK_O = 3.0, cation to free base; pK_S = (4.4) (approximate) cation to free base; pK_{R_1} = 1.0, cation to free base; pK_{R_2} = 10.1, free base to anion. The one anionic ionization of the semiquinone and the second in the reductant, which might occur at the hydrogens added by the reduction, were not evident in the pH regions investigated.

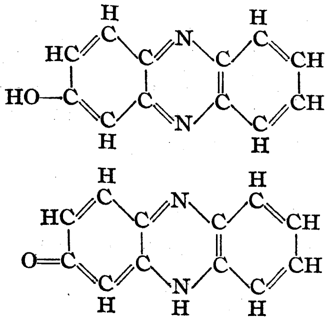


pH.

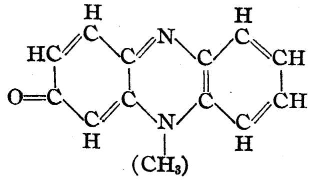
Fig. 2.

Only approximate values for the ionization constants for the semiquinones could be estimated, because the titration curves did not show a sufficiently high "index potential" to locate precisely the E_0' againts pH curves for the systems involving semiquinones. The effect of an ionization of a semiquinone is to change the solpe of the oxidant–semiquinone curve exactly to the same amount and in the opposite direction as the slope of the semiquinone-reductant curve, thereby causing no change in the slope of the resultant oxidant–reductant curve and preventing the detection there of any semiquinone ionizations.

The structure of β-hydroxyphenazine indicates that the oxidation–reduction system could involve either the two nitrogens or the oxygen and the nitrogen para to it. In the case of the N-methyl derivative, only one structure is possible, assuming that the methyl group does not have the power to shift its position.



β-Hydroxyphenazine



N-Methyl-β-oxyphenazine
(methylaposafranone)

Pyocyanine, N-methoxyl-α-oxyphenazine, and α-hydroxyphenazine have a similar relationship involving the ortho positions. The semiquinones in these cases have one additional hydrogen atom or electron, and the reductants two. The oxidants and reductants have the same structural relationship as quinone-imine to aminophenol; the structure of the semiquinones is discussed in the literature cited.[2,3]

In buffers at *p*H 6, the region of lowest semiquinone formation and where the un-ionized forms predominate, the E_0' of N-methyl-α-oxyphenazine is about 0.125 volt more positive than the E_0' of N-methyl-β-oxyphenazine. This amount is greater than the separation, 0.088 volt, of the ortho-quinone and the para-quinone systems, indicating that they are probably related as ortho–para isomers. The difference between the α- and the β-hydroxyphenazine is only 0.030 volt and they lie in the same general region where the E_0' of phenazine[6] would be expected, so that they are probably behaving as hydroxy substituted phenazines.

The low solubility and lack of contrasting color changes makes β-hydroxyphenazine unsuitable as a colorimetric indicator of oxidation–reduction potential. N-Methyl-β-oxyphenazine is useful as an indicator of oxidation–reduction potential from *p*H 5.5 to 12 in a zone about 0.05 volt more negative than that of indigo disulfonate, changing from red to colorless or light yellow, and as an indicator of hydrogen ion concentration in the acid region from about *p*H 2 to 4, changing from yellow to red. Because of the similarity of the color changes, care must be exercised, when it is used as an indicator, to distinguish one change from the other by suitably adjusting conditions in the material to be tested.

Summary

The oxidation–reduction potentials of β-hydroxyphenazine and N-methyl-β-oxyphenazine have been determined by an electrometric method and the ionization constants of the oxidants and of the reductants have been calculated from the data. The N-methyl-β-oxyphenazine has properties suggesting its use as an indicator for oxidation–reduction potential and for hydrogen ion concentration. The chemical structure of the compounds and certain theoretical aspects of semiquinone formation and oxidation–reduction potentials are discussed.

ST. LOUIS, MO. RECEIVED OCTOBER 9, 1936

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[6] L. Michaelis and E. S. Hill, THIS JOURNAL, **55**, 1493 (1933).

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

The Heat Capacity and Entropy of Rhombic and Monoclinic Sulfur

BY E. D. EASTMAN AND W. C. MCGAVOCK

The only data at present available in the literature on the heat capacity at low temperatures of the two crystalline forms of sulfur are early measurements made in Nernst's laboratory.[1] As these are insufficient for the determination of entropy with the certainty now desirable, we have made a more complete investigation, the results of which are presented here.

Experimental Details

The method of measurement of heat capacity was the standard one of electrical heating in vacuum now universally employed for such measurements at low temperatures, and conformed, in general practice, with that of numerous other investigations in this Laboratory at the date of these measurements, 1932–1933.

The calorimeter was constructed of gold, to enable measurements to be made near the transition temperature without danger of reaction of the metal with sulfur. It was welded from gold sheet of 1 mm. thickness in the form of a cylinder 7 cm. long and 5 cm. in diameter. Eleven radial vanes 0.2 mm. thick and extending nearly to the center were welded to the interior wall to promote thermal conduction. The opening to the calorimeter was provided by a tube of *einschmilzungsglas* sealed to a platinum tube which in turn was welded to the calorimeter. The materials of the calorimeter comprised 306 g. of gold, 3.66 g. of platinum and 5.52 g. of glass, together with small amounts of Bakelite lacquer and lens paper used in cementing and insulating the heater.

The calorimeter heater, which also served as a resistance thermometer, was of No. 40 B. and S. gage double silk insulated wire of gold alloyed with 0.1% silver, drawn in the manner described by Onnes and Clay.[2] Its resistance was 13.9 ohms at 15°K. and 248 ohms at 298°K. The procedure in attaching the heater-thermometer to the calorimeter was as follows. The surface of the calorimeter was first given a "hair" finish with fine emery paper. Two very thin coats of Bakelite lacquer were next applied, each dried in air and heated slowly in the course of a day or more up to 140–150°. This temperature was maintained until the color was a dark reddish-brown. A thickness of lens paper was then applied, the heater wound on, another thickness of lens paper applied and the whole soaked with Bakelite lacquer. This was baked as described above, and two or three more very thin coats of Bakelite applied. The surface was then covered with gold beaters leaf to cut down radiation interchange during the measurements.

The resistance thermometer on the calorimeter was standardized by comparison with a thermocouple which had been calibrated by Dr. R. T. Milner by comparison with laboratory standards, the temperature scale being that established by Giauque, Buffington and Schulze.[3] For the extension of this scale to higher temperatures the couple was calibrated at the transition temperature of sodium sulfate decahydrate and at the boiling point of water.

The timer described by Johnston[4] was used to measure the heating interval to less than one hundredth of a sec. The time of heating was from six to twenty minutes, the temperature increments varying from 1° at the lowest temperature to 6 or 8° near the transition.

A lead block of large heat capacity surrounded the calorimeter, making it possible to stabilize temperatures at points intermediate between those of the outer baths employed in different temperature ranges. For work above room temperature the metal can enclosing the block was provided with a heating coil for regulation of its temperature.

Helium at 75 cm. pressure at 20° was employed in the calorimeter to promote heat conduction to the sample. Measurements of the temperature head between the calorimeter wall and the sulfur showed it to be less than one-fifth the head between the heater and the wall (0.2 to 0.5°) under the same conditions.

Thermal equilibrium, except for a second order drift apparent between 200 and 300°K.,[5] was complete in the full calorimeter within ten or fifteen minutes after the heating period.

The calorimeter contained 113.41 ± 0.01 g. of sulfur prepared as follows. A pure crystallized commercial product was melted and maintained at 120° for several hours. It was then distilled in Pyrex glass and the distillate dissolved in freshly distilled carbon disulfide and recrystallized. Unbroken crystals, which passed a sieve opening of 3.5 mm. and were retained on a 2.0-mm. screen, were selected. These were freed of carbon disulfide by heating at 85 ± 5° at 1-mm. pressure for eight days. After this period, a test made by boiling a sample in a high vacuum resulted in the liberation of an amount of gas corresponding to less than 0.001% CS_2. All determinations on rhombic sulfur were made with this material. Monoclinic sulfur was obtained by holding the sample in the calorimeter at temperatures between the transition and melting points for a long period, as described later. The sample was never melted after the treatment above and could therefore have contained none of the "insoluble" sulfur, which differs considerably in heat capacity from monoclinic and is present in small amounts in material prepared by crystallization of the melt.

The data given below are based on the following constants: atomic weight of sulfur = 32.06, 1 cal. = 4.1833 int. joule, and 0 = 273.1°K.

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(1) (a) Nernst, Koref and Lindemann, *Sitzb. kgl. preuss. Akad. Wiss.*, 247 (1910); (b) Nernst, *Ann. Physik*, [4] **36**, 395 (1911).

(2) Onnes and Clay, *Leiden Communications*, **99c**, 21 (1907).

(3) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

(4) Johnston, *J. Opt. Soc. Am.*, **17**, 381 (1928).

(5) We suspect the glass sealing tube, because of its low thermal conductivity, to have been in part responsible for this drift. The large radiating and absorbing power is an additional unfavorable property of this material. We now consider all metal construction preferable.

Heat Capacity of Rhombic Sulfur

The results of the heat capacity measurements for rhombic sulfur are listed in Table I and shown graphically in Fig. 1. The figure also includes certain points from Table V, to be explained later.

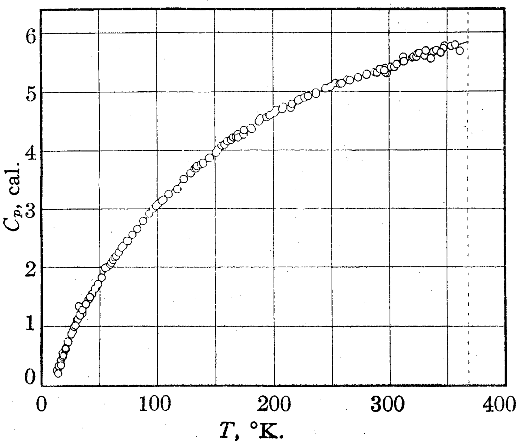

Fig. 1.—Atomic heat capacity of rhombic sulfur.

Table I

Atomic Heat Capacity of Rhombic Sulfur

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
12.68	0.254	122.76	3.508	249.02	5.081
13.85	.204	128.63	3.608	253.63	5.145
14.26	.331	132.02	3.684	257.12	5.130
16.13	.424	133.29	3.693	258.85	5.141
16.33	.341	134.02	3.728	263.79	5.202
17.99	.494	137.45	3.758	265.98	5.190
18.16	.505	139.32	3.790	272.91	5.240
20.26	.617	139.63	3.774	280.15	5.284
20.27	.631	144.50	3.863	280.47	5.296
22.23	.741	145.01	3.869	287.32	5.333
22.61	.732	150.39	3.953	289.12	5.325
25.18	.863	150.40	3.957	289.26	5.320
26.38	.917	150.40	3.957	290.17	5.382
28.66	1.012	152.21	4.013	295.48	5.361
30.71	1.114	155.44	4.079	296.46	5.323
32.62	1.182	157.92	4.095	296.55	5.401
34.68	1.274	160.16	4.155	297.71	5.314
37.70	1.374	163.26	4.176	298.28	5.362
41.10	1.494	165.08	4.210	301.40	5.419
45.79	1.642	165.31	4.219	302.32	5.414
51.39	1.826	167.75	4.227	303.97	5.415
55.93	1.966	169.16	4.274	306.13	5.466
58.95	2.045	169.50	4.217	311.46	5.508
59.82	2.078	174.26	4.267	311.95	5.586
62.54	2.167	174.76	4.342	312.42	5.513
63.99	2.189	180.25	4.378	319.98	5.577
66.33	2.250	181.33	4.361	320.92	5.593
68.84	2.336	187.56	4.492	323.17	5.590
70.04	2.357	188.86	4.543	324.37	5.648
70.34	2.367	194.00	4.562	325.87	5.653
73.22	2.453	196.67	4.598	330.34	5.608
74.04	2.455	200.83	4.642	331.32	5.690
74.61	2.452	202.25	4.688	335.76	5.558
78.12	2.554	207.38	4.701	338.11	5.674
82.44	2.654	208.25	4.740	340.22	5.697
87.66	2.791	214.59	4.730	344.16	5.657
92.81	2.915	215.69	4.794	346.87	5.728
96.29	2.989	220.99	4.851	347.86	5.773
98.83	3.045	222.50	4.868	353.74	5.765
100.83	3.086	226.56	4.900	357.23	5.789
103.92	3.136	229.53	4.925	361.21	5.681
105.25	3.154	236.46	4.959	364.02	5.935[a]
109.80	3.248	236.51	4.984	364.59	5.672[a]
117.13	3.346	244.79	5.056	365.60	5.944[a]

[a] In each of these runs the average temperature of the heater on the calorimeter was above the transition point of sulfur during a portion of the run. These points are not plotted in Fig. 1.

The individual measurements show fluctuations larger than can be attributed to instrumental errors, which in general were of the order of 0.1%. The very large differences among the points at the lowest temperatures result from inaccuracies in three separate calibrations[6] of the resistance thermometer in different series of experiments. These calibrations permit measurements of temperature differences in very close agreement over most of their range but deviate in the region of extremely small resistances. The remaining variations we believe to be due to imperfect drift and heat exchange corrections. At the highest temperatures employed, the method of measurement is inherently defective in this regard for precise work. In the intermediate range the difficulty attributed above to the glass tube on the calorimeter is important. To ensure the absence of constant errors from these sources in the final results, the conditions of approach to thermal equilibrium were varied systematically in making measurements. This, together with the large number of observations, gives us confidence in the accuracy of the averaged results, within the limits estimated below.

Representative values of the heat capacity read from the smoothed curve of Fig. 1 are given in Table II. The uncertainty connected with these smoothed values varies with the temperature. We estimate it to be about 8% at 15°K., 1.5% at 20°K., 1.0% at 30°K., and 0.5% at 40°K. From 60 to 290°K. it is of the order of 0.3%. Above 290°K. it averages about 0.5%. These figures are limits of error, which we think should not be exceeded in any values listed in Table II, with the possible exception of those very near the extremes of the temperature range.

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(6) Necessitated by changes in resistance resulting from the thermal treatment.

TABLE II

ATOMIC HEAT CAPACITY OF RHOMBIC SULFUR, SMOOTHED VALUES

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
15	0.311	200	4.639
20	.605	210	4.743
25	.858	220	4.841
30	1.075	230	4.927
40	1.452	240	5.010
50	1.772	250	5.083
60	2.084	260	5.154
70	2.352	270	5.220
80	2.604	280	5.286
90	2.838	290	5.350
100	3.060	298.1	5.401
110	3.254	300	5.412
120	3.445	310	5.474
130	3.624	320	5.535
140	3.795	330	5.598
150	3.964	340	5.660
160	4.123	350	5.721
170	4.269	360	5.783
180	4.404	368.6	(5.837)
190	4.526		

Comparison with the data of Nernst[1] shows our results in Table II to be lower by amounts varying from 6 to 28% between 20 and 30°K. and from 1 to 5% between 70 and 90°K. and near 200°K. The remaining data in the literature are all mean specific heats over large temperature intervals above room temperature due to Regnault,[7] Kopp,[8] Bunsen,[9] Wigand,[10] Koref,[1,11] Lindemann,[1] and Mondain-Monval.[12]

Our values are higher by amounts averaging about 2% than those of Kopp, Bunsen, and Mondain-Monval, and lower by about the same amount than those of the other observers.

The heat capacity at constant volume as a function of temperature is of some interest, and is approximately calculable in the case of rhombic sulfur. For this purpose the thermodynamic relation

$$C_p - C_v = \alpha^2 VT/\beta \qquad (1)$$

is employed. Based on the work of Kopp,[13] Russner,[14] and Schrauf,[15] we take the cubic coefficient of expansion at 20° as $\alpha = (18.1 \pm 1) \times 10^{-5}$ deg.$^{-1}$. The compressibility, β, from the work of Richards[16] and an extrapolation of Bridgman's data,[17] is $(13.0 \pm 0.2) \times 10^{-6}$ cm.^{2}/kg. at 20°. The atomic volume is 15.60 ± 0.05 cc. These values substituted in equation 1 give $C_p - C_v = 0.270 \pm 0.03$ cal./deg. at 20°. The value of C_p at this temperature from the smoothed curve of Fig. 1 is 5.37 ± 0.03. C_v at 293.1°K. is therefore 5.10 ± 0.05. Data required for application of equation 1 at lower temperatures are lacking. We have therefore resorted to an approximate empirical equation proposed and discussed by Grüneisen,[18] namely

$$C_p - C_v = kTC_p^2 \qquad (2)$$

From the datum above, k in this equation is found to be 3.20×10^{-5}. Employing this constant with figures for C_p from our work we obtain values of $C_p - C_v$ and C_v shown at regular intervals in log T in Table III.

TABLE III

CALCULATED ATOMIC HEAT CAPACITY AT CONSTANT VOLUME OF RHOMBIC SULFUR

Log T	$C_p - C_v$ cal./deg.	C_v cal./deg.
2.500	0.308	5.21
(2.4672)	(.270)	(5.10)
2.400	.208	4.88
2.300	.137	4.49
2.200	.085	4.00
2.100	.051	3.50
2.000	.0297	3.02
1.900	.0170	2.56
1.800	.0095	2.16
1.700	.0050	1.77
1.600	.0027	1.45

We may mention at this point that the values of C_v in Table III (and at lower temperatures where C_v is nearly identical with C_p) may be represented approximately up to $C_v = 3.0$ by the function

$$C_v = f(T/\Theta)^n \qquad (3)$$

proposed by Lewis and Gibson,[19] if $\log \Theta = 1.992$ and $n = 0.5025$. Above $C_v = 3.0$ deviations begin, C_v at 293°K. falling about 0.45 cal./deg. above the typical curve of these authors. Applying the values of n and Θ adopted by Lewis and Gibson to our data, we find that the experimental points fall above their curve at low temperatures and below it in the upper range by amounts much greater than the experimental error. No values of the constants applied to our

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[7] Regnault, *Pogg. Ann.*, **51**, 225 (1840); **62**, 50 (1844); *Ann. chim. phys.*, [2] **73**, 50 (1840); [3] **9**, 322 (1843).

[8] Kopp, *Liebigs Ann. Chem. Supp.*, **3**, 1 (1864–65).

[9] Bunsen, *Pogg. Ann.*, **141**, 1 (1870).

[10] Wigand, *Ann. Physik*, [4] **22**, 64 (1907).

[11] Koref, *ibid.*, [4] **36**, 49 (1911).

[12] Mondain-Monval, *Bull. soc. chim.*, [4] **39**, 1349 (1926).

[13] Kopp, *Ann.*, **93**, 129 (1855).

[14] Russner, *Carl Repert.*, **18**, 152 (1882).

[15] Schrauf, *Z. Kryst.*, **12**, 322 (1887).

[16] Richards, THIS JOURNAL, **37**, 1643 (1915).

[17] Bridgman, *Proc. Am. Acad. Arts Sci.*, **62**, 207 (1927).

[18] Grüneisen, *Ann. Physik*, **26**, 211, 393 (1908).

[19] Lewis and Gibson, THIS JOURNAL, **39**, 2554 (1917).

data will reproduce this curve over the full range of our investigation.

Heat Capacity of Monoclinic Sulfur

After completion of the runs with rhombic sulfur, the sample was transformed to monoclinic by maintaining the temperature of the calorimeter between 96 and 100° for a period of twenty-four hours. The first measurement recorded in column 4 of Table IV was then made, the calorimeter held for an additional twenty-four hours above the transition point and the second measurement made. During these runs the conditions appeared as nearly ideal as could be obtained, and they were therefore considered sufficient to establish the heat capacity of the monoclinic form in the rather narrow range of temperature within which it is stable. After the second run, the calorimeter was cooled as rapidly as possible to 60°K. The initial rate of cooling was 10° per minute, and in thirty minutes the temperature was reduced to 200°K., below which transition is very slow. Runs numbered 3 to 16 in Table IV were then made in sequence. The total time elapsing from the beginning of the initial cooling to the start of the run is shown in each case in the second column of the table. After completion of run 15 the temperature was raised to about 218°K. and maintained there for fifty-three hours before the start of run 16. Following this the calorimeter was again cooled, and run 17 completed at 92°K. Immediately before run 18 the calorimeter was heated from this temperature to about 153°K.

Table IV

Atomic Heat Capacity of Monoclinic Sulfur, and its Difference from that of Rhombic Sulfur

Run no.	Time, hours	Temp., °K.	C_p, cal./deg.	ΔC_p, cal./deg.	$(\Delta C_p/T) \times 10^4$ cal./deg.
1	...	376.16	6.175	0.292	7.76
2	...	375.14	6.167	.291	7.76
3	3	64.83	2.242	.0198	3.05
4	7	68.82	2.330	.0045	0.66
5	9	72.82	2.431	.0045	0.62
6	24	80.12	2.622	.0220	2.75
7	27	84.76	2.744	.0265	3.13
8	96	94.31	2.976	.0330	3.50
9	97	98.25	3.069	.0435	4.43
10	139	102.55	3.150	.0401	3.91
11	144	110.08	3.293	.0381	3.46
12	161	119.59	3.481	.0404	3.38
13	180	127.24	3.642	.0599	4.71
14	193	147.42	4.028	.1118	7.59
15	211	172.41	4.404	.0972	5.64
16	264	219.80	4.930	.0895	4.07
17	288	91.98	2.641	.0282	3.07
18	334	154.91	4.158	.1136	7.33

The results shown in Table IV lie consistently above the smoothed curve for the rhombic form. Runs 18 and 19, at 92 and 155°K., respectively, which were made after the calorimeter had been held for a long period at 220°K., agree within the experimental error with the preceding runs near these temperatures. We have taken this as evidence that no appreciable reversion to the rhombic form occurred in this series after the initial cooling. Run 17 at 220° appears to be rather lower than should correspond to the monoclinic form at this temperature. We have indications from later runs, however, that this is due to an unusually large fluctuation rather than to transition, and consequently attach less weight to this point than to the others.

In an attempt to confirm and extend the data on the monoclinic form, the sample, which had been allowed to warm and stand for some days at room temperature, was again heated and held above the transition point, and then cooled rapidly, this time to 12°K. A second series of measurements ranging from 13.5 to 205°K. was then made. At temperatures where the two forms differ appreciably in heat capacity, as shown by the earlier measurements, this series gave results only a little higher than those with rhombic. We believe that the repetition of the transformation had produced more reactive crystals, in which the transformation could not be so completely inhibited on cooling as with those which had undergone only the single change. (It should be mentioned that during the "annealing" period preceding the cooling an accidental drop below the transition temperature occurred, which may have had some influence on the subsequent behavior.) In connection with this point, the appearance of the sample after removal from the calorimeter may be noted. The crystals, which had been subjected to several transitions, had maintained their original form, but had become opaque, indicating the presence of small crystals in mosaic form.

Of the measurements of this series, only those below 65°K., which are useful in supplementing the data on rhombic sulfur, with which they are identical within the errors in this range, will be recorded here. These are given in Table V, and plotted in Fig. 1.

A third "annealing" above the transition tem-

TABLE V

ATOMIC HEAT CAPACITY OF A MIXTURE OF MONOCLINIC AND RHOMBIC SULFUR

T, °K.	C_p
13.51	0.217
15.41	.326
17.75	.549
18.65	.538
20.27	.621
22.72	.739
25.38	.874
27.73	.993
29.99	1.106
32.33	1.199
34.66	1.213
36.55	1.338
39.86	1.446
43.04	1.550
48.17	1.717
54.19	1.994
61.43	2.127

perature was next made, followed by a series of runs extending from 110 to 345°K. The results of these measurements in the lower temperature range fell consistently between the rhombic curve and the first series of points for the monoclinic. From their position relative to these two, it appeared that the sample consisted in this case of about 60% of the monoclinic form. The corresponding difference in heat capacity persisted up to 255°K. Within the period of ten hours intervening between the run at this temperature and the next at 268°K., the sample was apparently entirely transformed to rhombic, since its heat capacity fell to the rhombic curve and remained there in all succeeding runs. No further attempts to secure measurements on monoclinic sulfur were made.

The evidence cited above convinces us that no appreciable conversion of monoclinic to rhombic occurred after the initial cooling in any of the three series of experiments at temperatures below about 250°K. During the cooling itself there was marked conversion in the second and third series. We believe that if any such effect occurred in the first series it could have affected only a small fraction of the sample. The approximate agreement of our results, discussed below, for the difference in heat capacity of the two forms with those of Nernst near 200°K. supports this belief, since Nernst's observations were made on relatively large crystals of monoclinic sulfur which were known not to transform appreciably on cooling.

We consider it advantageous for the present purposes in dealing with the data on monoclinic to treat the difference, ΔC_p, of monoclinic from rhombic, rather than C_p itself. Values of ΔC_p (and of $\Delta C_p/T$) from our work are therefore included in Table IV. These are computed from the difference in heat capacity of the full calorimeter in individual runs with monoclinic sulfur from the smoothed curve for the full calorimeter containing rhombic sulfur at the same temperature. We have secured smoothed values of ΔC_p, and at the same time obtained a plot for use in a later calculation, by treating $\Delta C_p/T$ as a function of temperature.

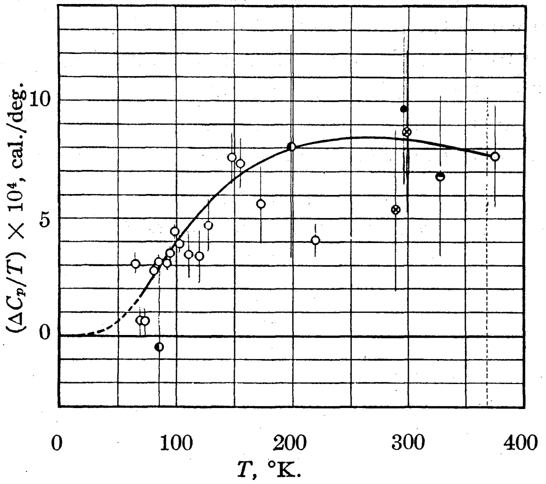

Fig. 2.—Difference of atomic heat capacities of monoclinic and rhombic sulfur: Regnault, ⊖; Wigand, ⊗; Nernst, ◐; Koref, ●; this research, ○.

In Fig. 2, $\Delta C_p/T$ is plotted against T. The vertical strokes attached to points representing our measurements are intended to give an idea of the experimental uncertainty. They represent the average deviation of three or four determinations on rhombic sulfur from the smoothed curve for rhombic immediately above and below the temperature of the monoclinic run in question. The uncertainty in particular cases may therefore exceed considerably that indicated as normal. For comparison with our results, and to supplement them, values of ΔC_p obtainable from the work of other observers are also plotted in Fig. 2. These data represent small groups of points at neighboring temperatures for the two forms which have been corrected to a common mean temperature, averaged separately, and the difference of the averages plotted against the mean temperature. Our estimate of the uncertainty is also indicated for these points in the plot.

The curve shown in Fig. 2 fits all of the points within the experimental uncertainty, and is correct in general form. The approximate position and shape of the theoretically required maximum in the curve we have inferred from the position of our points above the transition temperature relative to the fairly well defined course of the curve at low temperatures, and also from the points of the third series of measurements mentioned above. From the curve as shown we have obtained smoothed values of ΔC_p. These, in conjunction with the data of Table II on rhombic, yield smoothed values of C_p for monoclinic sulfur shown in Table VI over the temperature range in which the difference in heat capacity of the two forms is significant. The uncertainty in C_p in this table is of the order of 1.5% in the upper temperature range, and approaches that previously estimated for rhombic at lower temperatures.

Table VI

Atomic Heat Capacity of Monoclinic Sulfur ("Best Values")

T, °K.	ΔC_p, cal./deg.	C_p monoclinic, cal./deg.
60	0.007	2.091
80	.020	2.624
100	.040	3.100
120	.063	3.508
140	.087	3.882
160	.112	4.235
180	.136	4.540
200	.159	4.798
220	.180	5.021
240	.199	5.209
260	.217	5.371
280	.234	5.520
298.1	.248	5.649
300	.250	5.662
320	.264	5.799
340	.276	5.936
360	.286	6.069
368.5	.289	6.126

Calculations of Entropy

The entropy difference between 15°K. and any higher temperature up to the transition point for rhombic sulfur is obtainable by graphic integration on a suitable plot of the data of Table II. For the entropy difference between 0 and 15°K., we find by similar integration under an extrapolated curve of C_p/T against T, and by calculation from a Debye function fitted to our points up to 40°K., 0.12 ± 0.02 e. u. For the total entropy of rhombic sulfur we obtain 7.624 ± 0.05 e. u. at 298.1°K. and 8.827 ± 0.06 at the transition point (368.6°K.).

The entropy of transition of rhombic to monoclinic sulfur is determined by integration under the curve in Fig. 2 to be 0.157 ± 0.04 e. u. at 298.1°K. and 0.215 ± 0.05 at 368.6°K. By combination of these figures with the values for the rhombic form, the entropy of monoclinic sulfur is 7.78 ± 0.1 e. u. at 298.1°K. and 9.04 ± 0.1 e. u. at 368.6°K.

These results are in agreement with those of Lewis and Gibson,[19] 7.6 and 7.8 e. u. at 298.1°K., for the two forms. The closeness of this agreement is in part fortuitous, in view of our earlier remarks in the discussion of C_v. Equally well justified calculations of the type of Lewis and Gibson's might introduce discrepancies of the order of 0.5 e. u. To this degree of approximation, however, their method is justified in the case of sulfur.

For comparison of the above value of ΔS obtained by application of the third law with one based solely on the second law, existing data on the heat of transition may be employed. Numerous measurements of ΔH, by widely different direct and indirect methods, due to Mitscherlich,[20] Reicher,[21] Tammann,[22] Brönsted,[23] Mondain-Monval,[12] and Neumann[24] are available. After a critical review of the work of these investigators, into which we cannot enter here, we have adopted 95 ± 10 cal. as the value of ΔH at the transition point. This corresponds to 0.258 ± 0.027 e. u., compared with the value based on the third law of 0.215 ± 0.05 at the same temperature.

It appears from this comparison that the third law is accurately applicable, without complications of the types that sometimes occur, to the sulfur transition. The uncertainty of 0.05–0.1 e. u. in this "check" of the law is smaller[25] than that in many others, and permits the assumption of no significant discrepancy. This case, as is well known, has often been cited in support of the third law. The experimental basis for this claim is greatly strengthened by the data discussed here.

Summary

Measurements of the heat capacity of rhombic and monoclinic sulfur have been made over the temperature range 15–375°K., and from them the

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[20] Mitscherlich, *Pogg. Ann.*, **88**, 328 (1852).

[21] Reicher, *Z. Kryst.*, **8**, 593 (1884).

[22] Tammann, "Kristallisieren und Schmelzen," Barth, Leipzig, 1903, p. 274.

[23] Brönsted, *Z. physik. Chem.*, **55**, 371 (1906).

[24] Neumann, *ibid.*, **A171**, 416 (1934).

[25] It is, of course, the absolute rather than the percentage figure which is important in such tests.

entropy of both forms determined. The entropy difference of the two forms obtained from the heat capacities agrees, within the small experimental uncertainty, with that from the heat of transition, as expected from the third law.

The heat capacity at constant volume has been calculated for rhombic sulfur, and its variation with temperature compared with the "*n* formula" of Lewis and Gibson.

BERKELEY, CALIF. RECEIVED NOVEMBER 10, 1936

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

The Reaction of Titanium Tetrachloride with Hydrogen Peroxide in Dry Ethyl Acetate

BY DOUGLAS G. NICHOLSON AND M. ANTOINE REITER

Several references concerning addition compounds of titanium tetrachloride and neutral molecules have appeared in recent chemical literature.[1–4] In view of these references, it seemed quite probable that titanium tetrachloride would unite with hydrogen peroxide in a non-aqueous medium to form a similar addition compound. Since both substances have an appreciable solubility in dry ethyl acetate, this material was selected as the solvent in the investigation.

Experimental

The solution of hydrogen peroxide in dry ethyl acetate was prepared in a manner previously described.[5] This peroxide solution was added slowly to an ice cold solution of titanium tetrachloride in ethyl acetate. As it was added, the titanium solution became orange to orange-red in color, and, with continued addition of the peroxide, a white crystalline precipitate formed. After thoroughly washing this precipitate with cold dry ethyl acetate, samples were analyzed in an effort to determine the chlorine to titanium, as well as the hydrogen peroxide to titanium, ratios present. Efforts to determine the actual composition of the white precipitated material proved unsatisfactory, because of its extremely unstable nature.

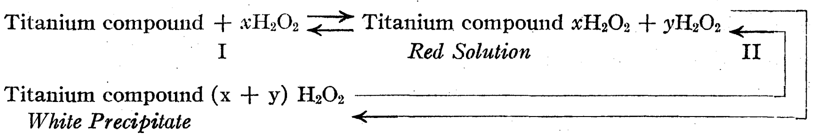
Data

Analysis of fourteen different samples of the material showed the average ratio of chlorine to titanium content to be 1 to 1.05 with an average deviation of 0.01 and a maximum deviation of 0.03. The average hydrogen peroxide to titanium ratio obtained from the same sample was 1 to 1.01 with an average deviation of 0.022 and a maximum deviation of 0.05.

Discussion

The color change encountered, as the solution of hydrogen peroxide in acetate was added to the titanium tetrachloride solution, followed by the formation of the white precipitate, seemed to indicate that more than one compound of these two substances had been formed. If some of the red colored solution was allowed to remain in an open vessel for some time the intensity of the color gradually faded.

In view of these facts the following equilibria are postulated:



The presence of a trace of moisture caused the white precipitate to become orange-red in color. Thus, it seems quite probable that moisture tends to shift the right-hand equilibrium (II) toward the left. All attempts to remove the last traces of acetate solution from the white precipitate resulted in its partial decomposition, in which the surface of the material became yellow to orange in color. This white precipitate was very soluble in water, producing the yellow to orange typical peroxytitanate solutions.

Analysis of the titanium tetrachloride used showed it to be very pure. The apparent loss of three atoms of chlorine per molecule of titanium tetrachloride can be attributed to either or both of two factors: namely, (1) oxidation to free chlorine by the hydrogen peroxide present, and

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(1) Chrétien and Varga, *Compt. rend.*, **201**, 558 (1935).
(2) Ralston and Wilkinson, THIS JOURNAL, **50**, 258 (1928).
(3) Holtje, *Z. anorg. allgem. Chem.*, **190**, 241 (1930).
(4) Karantassis, *Compt. rend.*, **194**, 461 (1932).
(5) Nicholson, THIS JOURNAL, **58**, 2525 (1936).

(2) partial decomposition of the ethyl acetate, producing ethyl chloride and titanium acetate. The second factor seems more probable, since refluxing a solution of titanium tetrachloride in ethyl acetate resulted in a partial loss of chlorine. No explanation is made concerning the fact that but three of the chlorine atoms had been replaced.

Summary

The reaction between titanium tetrachloride and hydrogen peroxide in dry ethyl acetate has been studied in some detail. A white compound containing titanium, chlorine and hydrogen peroxide in the approximate ratio of 1:1:1 can be prepared. This material is unstable toward water, as well as slightly elevated temperatures. In decomposing, it becomes yellow-orange in color. It is very soluble in water, producing orange-red clear solutions.

URBANA, ILL. RECEIVED SEPTEMBER 16, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Use of Iodine and of Potassium Iodate as Volumetric Oxidizing Agents in Solutions Containing Mercuric Salts. I. The Effect of Mercuric Salts upon the Stoichiometry of Various Oxidation–Reduction Reactions. New Procedures for the Titration of Arsenite and Antimonite with Standard Solutions of Iodine or of Potassium Iodate

BY N. HOWELL FURMAN AND CLARK O. MILLER[1]

Introduction

The stoichiometry of certain reactions between powerful oxidizing agents and halides, or between the halogens or their oxy acids and reducing agents, is modified when mercuric salts are present in excess. Several situations may arise, depending upon particular halide that is present, the total acidity and the relative concentrations of mercuric salt, halide and acid. There are two principal kinds of behavior which are of interest here: (a) the failure of free halogen to appear when a limited quantity of a halide, an excess of mercuric ion and an excess of nitric, sulfuric or perchloric acid is treated with a powerful oxidizing agent, as for example, potassium bromate or permanganate; (b) the reduction of bromate to bromide, of iodate to iodide and of iodine to iodide by various reducing agents in the presence of an excess of mercuric salt and acid. The former case will be reviewed briefly with presentation of some experimental observations, and the latter will be treated more fully, especially with regard to the reactions of potassium iodate and of iodine and the application of these reactions in volumetric analysis.

(a) The Non-appearance of Free Halogen when Mercuric Salt is Present in Excess.—G. F. Smith[2] described a series of experiments in which solutions of bromides, chlorides or iodides containing mercuric nitrate or perchlorate and the corresponding free acid were heated with an excess of potassium bromate solution. He reported that no reaction was observed and that the solution after the heating liberated an amount of iodine equivalent to the original potassium bromate when an excess of potassium iodide was added to the cold solution. He found similar results for mixtures of a bromide, mercuric salt, potassium permanganate and acid, and attributed this "preventive effect" to the formation of slightly ionized mercuric halides.

We have repeated experiments of the type described by Smith upon mixtures containing potassium iodide, excess of mercuric sulfate and sulfuric acid. Potassium bromate or permanganate was added. After heating there was no loss of oxidizing power toward potassium iodide. Reactions had occurred, however, for the potassium bromate had been reduced and an equivalent amount of iodate had been formed, as was indicated by the presence of bromide and iodate in mixtures that were examined qualitatively and by quantitative experiments. The potassium permanganate was decolorized and iodate was formed. Smith's explanation[2] of the "protective action" of mercuric salts is contradicted by these qualitative experiments.

In the case of iodide, which is of principal inter-

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[1] Present address, Case School of Applied Science, Cleveland, O.

[2] G. F. Smith, THIS JOURNAL, **45**, 1417 (1923).

est in this paper, the oxidation proceeds to the iodate stage without visual evidence of the intermediate formation of free iodine when mercuric salts are present in sufficient excess. In the absence of mercuric salts the oxidation of iodide usually leads to the quantitative liberation of iodine in solutions that are 1–2 *N* in acid. The explanation of the effect of mercuric salts seems clear from the evidence that is available in the literature. In the oxidation of iodide to higher states we are concerned with the effect of mercuric ion and acidity upon the equilibria

$$2I^- + 2e \rightleftharpoons I_2 \quad (1)$$
$$I_2 + H_2O \rightleftharpoons I^- + IO^- + 2H^+ \quad (2)$$
$$3IO^- \rightleftharpoons IO_3^- + 2I^- \quad (3)$$

Measurements are presented in this paper regarding the effect of mercuric ions and acidity upon process (1). Mercuric ions tend to bind iodide ions in the form of complex and undissociated molecules. It is thus more difficult to liberate iodine from an iodide in the presence of a mercuric salt than in its absence. Mercuric ions tend to aid processes (2, 3) by removing one of the products of the reaction, namely, iodide. Some of the evidence previously published regarding processes (2, 3) in the presence of mercury will be summarized briefly. Brückner[3] found that iodine in the presence of mercuric oxide undergoes autoxidation

$$6HgO + 6I_2 = 5HgI_2 + Hg(IO_3)_2 \quad (4)$$

A similar autoxidation occurs if mercuric sulfate is added to a solution of iodine. A complex white precipitate that contains mercuric sulfate, iodide and iodate, is formed. Hovorka[4] observed a similar process when mercuric perchlorate was used.

$$6Hg(ClO_4)_2 + 6I_2 + 6H_2O = 5HgI_2 + Hg(IO_3)_2 + 12HClO_4 \quad (5)$$

This type of autoxidation is not limited to iodine, for Chateau[5] has demonstrated similar autoxidation of bromine and chlorine, respectively, in the presence of mercuric mercury, to form hypochlorite or hypobromite. The change of hypoiodous acid to an equivalent mixture of iodate and iodide (equation 3) is rapid according to Skrabal.[6] Reaction (2) is also rapid, for a solution of iodine is rapidly decolorized when added to a solution of mercuric sulfate.

The binding or removal of iodide ions is the important factor in promoting the change of iodine to iodate. A similar autoxidation occurs when silver is used instead of mercuric ion[7] and the mechanism has been shown to involve reactions (2, 3).

We have shown qualitatively that the presence of an excess of a mercuric salt does not inhibit the oxidation of a limited quantity of halide ion by a powerful oxidizing agent like potassium permanganate or potassium bromate. Evidence from the literature has been cited to show the mechanism of the formation of oxy-halogen acids by spontaneous autoxidation of the halogens in the presence of mercuric or silver ions. In a particular case such as the reaction between bromate and iodide, the presence of mercuric salt tends to establish an equilibrium between iodate, iodide, bromate and bromide such that the total oxidizing power of the solution toward a powerful reductant remains constant.

(b) **The Action of Reducing Agents upon Bromate and Iodate in the Presence of Mercuric Salts.** (1) **In the Presence of Mercuric Sulfate, Perchlorate or Nitrate and the Corresponding Acid.**—Under these conditions bromate is reduced to bromide or iodate to iodide by a reductant that is sufficiently powerful. The following are some typical reactions

$$6Mn^{++} + 2BrO_3^- + 6H_2O + Hg^{++} = 6MnO_2 + HgBr_2 + 12H^+ \quad (6)$$
$$4Cr^{+++} + 2BrO_3^- + 10H_2O + Hg^{++} = 4HCrO_4^- + HgBr_2 + 16H^+ \quad (7)$$
$$6NO_2^- + 2BrO_3^- + Hg^{++} = 6NO_3^- + HgBr_2 \quad (8)$$
$$6C_2O_4^= + 2BrO_3^- + Hg^{++} + 12H^+ = 12CO_2 + HgBr_2 + 6H_2O \quad (9)$$

In the absence of mercuric ion, the bromate is reduced to free bromine in each instance (6–9).

Hovorka[4] determined the lower acids of phosphorus and also certain hydrazine derivatives by adding a measured excessive quantity of standard potassium iodate, mercuric perchlorate and acid. After oxidation was complete the excess of oxidant was determined.

(2) **Reactions in the Presence of Mercuric Chloride.**—When chloride is present in excess, and mercuric ion is present, there is competition between iodide and chloride ion for association with mercuric ion in the form of complexes or nonionized molecules. There is also a distribution of any elementary iodine that may be present be-

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(3) K. Brückner, *Monatsh.*, **27**, 341 (1906); **28**, 961 (1907).

(4) Hovorka, *Collect. Czechoslovak Chem. Comm.*, **2**, 559, 608 (1930); **3**, 285 (1931).

(5) Chateau, *Bull. soc. chim.*, [4] **17**, 121 (1915).

(6) Skrabal, *Chem.-Ztg.*, **33**, 1184 (1909).

(7) Josien, *Ann.*, **11**, 5, 147 (1936); *cf.* also Kolthoff and Furman, "Potentiometric Titrations," J. Wiley & Sons, Inc., New York, 1931, p. 192.

tween combination with iodide ion and mercuric chloride, respectively. The net result of these various tendencies is that iodate tends to be reduced to iodide and iodine to iodide by the majority of reductants (those of E_0 values less than 0.5–0.6 volt). Iodine under these conditions shows no tendency to undergo autoxidation to form iodate and iodide. Mercuric iodide is readily soluble in a sufficient excess of hydrochloric acid, and it dissolves without decomposition according to Kohler.[8]

In the absence of chloride ion, mercuric salts such as the sulfate tend to form complex basic salts, most of which are insoluble.[9]

The presence of chloride ion and acid tends to diminish the "protective effect" that Smith[2] observed. The following table indicates the extent to which loss of halogen occurs under various conditions.

TABLE I

THE EFFECT OF CHLORIDES UPON THE REACTION BETWEEN IODIDE AND BROMATE IN THE PRESENCE OF MERCURIC NITRATE

20.00 ml. of approximately 0.1 *N* $KBrO_3$ used, equivalent to 23.15 ml. of approximately 0.1 *N* $Na_2S_2O_3$. Mercury added as HgO dissolved in HNO_3. Time of boiling five minutes. Dilution 100 ml. 10.0 ml. 0.1 *N* KI added. 2.0 g. of mercury in soln.

Expt.	NaCl added, g.	Nitric acid, *N*	Iodine value of boiled solns., ml. of $Na_2S_2O_3$	Difference ml. of $Na_2S_2O_3$
1	0.0	1.0	23.13	−0.02
2	.1	1.0	23.05	− .10
3	.2	1.0	22.95	− .20
4	.7	0.5	22.60	− .55
5	1.0	1.0	22.90	− .25
6	1.5	2.0	17.90	−5.25
7	2.0	1.0	20.25	−2.90
8	5 ml. 6 *N* HCl	0.5	20.20	−2.95
9	10 ml. 6 *N* HCl	1.0	17.75	−5.40

In expts. 1–5 there was insufficient chloride to bind the mercury completely as mercuric chloride (2 g. mercury is equivalent to 1.17 g. sodium chloride). The formation of a mercuric iodate precipitate was noted in expts. 1–3. Solutions 6–9 became brown showing the liberation of iodine.

If error were introduced by the action of nitric acid upon the iodide to liberate iodine it would be in the direction opposite to that found by experiment. After the heating, the solution was cooled and diluted to 250 ml. before the addition of excess of potassium iodide to avoid the liberation of excess iodine by the action of nitric acid after the protective action of the mercuric ion had been removed. Experiment 1 indicates that this procedure is adequate.

We attribute the loss in oxidizing power (expts. 2–8, Table I) to the fact that the iodine does not undergo immediate autoxidation in such solutions, and hence escapes as vapor.

The following differences between the behavior of iodine in neutral and acidified mercuric chloride solutions are rather striking, and confirm the view that hydrochloric acid prevents autoxidation of iodine.

(a) Concentrated mercuric chloride solution plus iodine.	(b) A mixture of 5 ml. saturated iodine solution, 10 ml. saturated $HgCl_2$ soln. and 40 ml. of 6 *N* HCl.
1. The color of iodine disappears, unless a rather large amount is added.	1. The iodine color is evident, but faint.
2. No iodine is extracted from the colorless solution by carbon tetrachloride.	2. Iodine is extracted, but with much greater difficulty than from water. After 4 extractions with 5 ml. portions of CCl_4 only half of the iodine had been removed from the soln.
3. Upon addition of HCl, iodine is liberated.	3. After extraction, no iodide could be detected in the aqueous layer. (Evidence of non-formation of ICl which should leave iodide in the aqueous layer, $I_2 + Cl^- = ICl + I^-$)
4. After the removal of iodide from the aqueous layer by silver ion, the remaining solution[a] was able to oxidize iodide when acidified with HCl.	4.[a] The iodine that remained in the aqueous layer could be titrated to iodine monochloride with standard iodate.
[a] At this point the solution contained iodate.	[a] At this point the solution contained iodine and not iodate.

In both cases (a, b) we are concerned with the gross process

$$6I_2 + 6H_2O + 6HgCl_2 = 5HgI_2 + Hg(IO_3)_2 + 12HCl \tag{10}$$

but in case (a) the equilibrium conditions are such that the formation of iodate is favored, whereas with excess of acid (case b) the interaction of iodate and iodide to form free iodine is favored. There is a further competing reaction that must be considered

$$HgCl_2 + I_2 \rightleftharpoons HgCl_2I_2 \tag{11}$$

as was found in distribution experiments by Herz and Paul.[10] This process accounts for the great difficulty with which iodine is extracted from solutions containing mercuric chloride and hydrochloric acid.

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(8) Kohler, *Ber.*, **12**, 608 (1879).

(9) In Gmelin-Kraut, "Handbuch der anorganische Chemie," Vol. V^2, pp. 804–805, many compounds of the type $(3HgO\cdot 2SO_3)_x\cdot HgI_2\cdot yH_2O$ are reported.

(10) Herz and Paul, *Z. anorg. Chem.*, **85**, 214 (1914).

In the foregoing considerations the formation of iodine monochloride has been neglected, although it might be an intermediate step in certain of the autoxidations that occur.[11]

Explanation of the Varied Stoichiometry of Iodate Reactions in the Presence of Mercuric Chloride and Hydrochloric Acid.—It has been demonstrated by Schoonover and Furman[12] that in addition to the customary iodate processes

$$IO_3^- + 6H^+ + Cl^- + 4e = ICl + 3H_2O \quad (12)$$

(In 4–6 *N* HCl; Hg may be either present or absent)

and

$$IO_3^- + 6H^+ + 5e = {}^1/_2I_2 + 3H_2O \quad (13)$$

(dilute acid, 1–3 *N*; Hg^{++} absent)

a third type of stoichiometry may be realized in the oxidation of arsenite by iodate ion

$$IO_3^- + 6H^+ + 6e = I^- + 3H_2O \quad (14)$$

The last process (14) occurs in the presence of a sufficient excess of mercuric chloride and at acidities between 1 and 3 *N*. In the subsequent section an attempt will be made to explain the latter type of stoichiometry upon the basis of electrode potential measurements.

The Effect of Mercuric Salts upon the Iodine–Iodide Potential

We now present measurements of the effect of mercuric salts upon the iodine–iodide potential, and make application of the effect to the titration of arsenite and antimonite by iodine at acidities not used hitherto.

In the measurements of potentials an attempt has been made to reproduce the conditions that prevail during titrations and to obtain data showing how the potentials of the various systems change relative to each other as a function of acidity. From such data it is possible to choose the most favorable range of acidity. No attempt has been made to correct for liquid junction potentials, since the calculation of the corrections at the high concentrations in question presents difficulties,[13,14] and for the present purposes relative potential values are adequate. As has been pointed out by Brönsted and Pedersen[15] high precision in measuring relative potentials is obtained when the concentration of the oxidation–reduction system is small relative to that of the other electrolytes.

As a test of our technique we have repeated the determination of the potential of the arsenate–arsenite systems as a function of acidity and have obtained good agreement with the data of Foerster and Pressprich[16] as is shown by the graph of the values on Fig. 1, curve 2, where points from both sets of measurements are plotted.

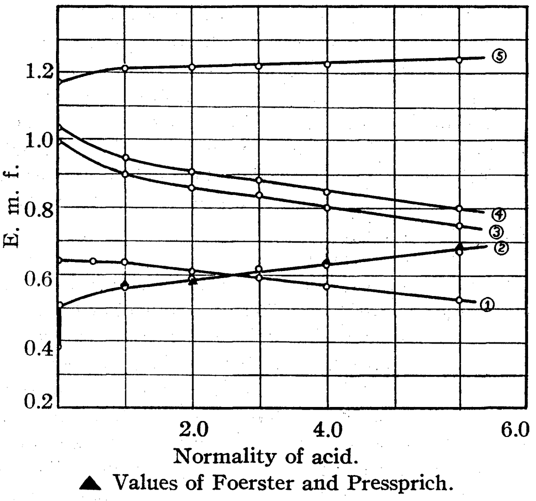

Fig. 1.—The abscissas represent normalities of hydrochloric acid, curves 1–5, or of sulfuric acid, curve 6. The ordinates represent oxidation–reduction potentials relative to the normal hydrogen electrode as zero, without correction for liquid junctions: (1), oxidation–reduction potentials of solutions 0.01 *N* in both iodine and iodide; (2), data for the arsenic system; solutions 0.01 *N* or 0.005 *M* in both forms of arsenic. The solid triangles are from measurements of Foerster and Pressprich:[7] (3), graph of potentials for the solutions used in (1) after adding 2 g. of mercuric chloride per 50 ml; (4), graph of potential values after adding 2 g. of mercuric chloride per 50 ml. of the solutions used in (3); (5), graph of potential values obtained upon adding 2 to 4 g. of solid mercuric sulfate to 50-ml. portions of solutions approx. 0.01 *N* in both iodine and potassium iodide and containing sulfuric acid as given on the abscissa axis.

Experimental

Apparatus and Materials.—Potentials were measured with a student-type assembly. Two spirals of bright platinum were used and averages of concordant readings of these relative to a saturated calomel electrode have been recorded. The side arm of the electrode terminated in a sintered porcelain plate. The cell was maintained at 25 ± 0.1° in a thermostat.

Potentiometric titrations were made by the classical

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[11] Faull and Forbes, THIS JOURNAL, **55**, 1809 (1933), postulate the formation of iodine monochloride in 6 *N* HCl solution by the action of air and light upon iodine. Hübl (cited in Beckurts "Methoden der Massanalyse," F. Vieweg and Sohn Braunschweig, 1931, p. 162) inferred that iodine monochloride was formed by the interaction of mercuric chloride and iodine in alcoholic solution.

[12] Schoonover and Furman, *ibid.*, **55**, 3123 (1933).

[13] Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

[14] Guggenheim, *ibid.*, **33**, 842 (1929).

[15] Brönsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

[16] Foerster and Pressprich, *Z. Elektrochem.*, **33**, 176 (1927).

method[17] or by the Furman and Wilson[18] continuous reading method. The calibrations of measuring vessels, standard cells and weights were checked against the secondary laboratory standards. Arsenious oxide from the Bureau of Standards was the basis of standardization of the volumetric solutions.

A solution approximately 0.02 *N* in iodine and in potassium iodide was prepared by dissolving 2.8806 g. of resublimed iodine and an equivalent amount (3.7678 g.) of dried reagent grade potassium iodide and diluting to 1 liter. An arsenate-arsenite solution of similar concentration was prepared from 1.0682 g. of reagent grade arsenious oxide dissolved in a minimum amount of sodium hydroxide, plus an equivalent amount (4.337 g.) of recrystallized sodium arsenate ($Na_2HAsO_4 \cdot 12H_2O$). The solution was made faintly acid to phenolphthalein and diluted to 1 liter.

Solutions of arsenite and antimonite for testing new titration procedures were prepared from Merck reagent grade arsenious oxide or from tartar emetic from the J. T. Baker Chemical Co., and analyzed iodometrically. Mercuric chloride was added in the form of a saturated solution in *N* hydrochloric acid.

Potential Measurements.—Twenty-five-ml. portions of the iodine–iodide solution were pipetted into the cell and the solution was diluted to 50 ml. with acid of the proper concentration to make the final concentrations as indicated in Table II. No attempt has been made to introduce corrections for triiodide ion formation because mercuric chloride is capable of binding both iodide ion and free iodine (or triiodide) to varying extents at various acidities. After making measurements on various mixtures of iodine–potassium iodide–acid, in each case 2 g. of solid mercuric chloride was added, and the mixture was stirred to constant composition and potential. The process was then repeated with the addition of 2 g. more of mercuric chloride. The data are recorded in Table II.

Table II

The Effect of Hydrochloric Acid and of Mercuric Chloride upon the Iodine–Iodide System at 25°

	Potential, Pt *vs.* satd. calomel, v.		
HCl, *N*	1 Soln. 0.01 *N* in I_2 & KI	2 As in 1 plus 2 g. $HgCl_2$ per 50 ml.	3 As in 2 plus 2 g. $HgCl_2$ per 50 ml.
0.0	0.400	0.760[a]	0.787[a]
.5	.400	.687[a]	.721[a]
1.0	.395	.662	.692
2.0	.376	.628	.649
3.0	.362	.607	.625
4.0	.345	.586	.604
6.0	.294	.531	.546

[a] In these instances a little solid iodine was observed. To each of the values (col. 1–3) 0.246 volt has been added in plotting Fig. 1.

A similar series of measurements was made upon solutions containing mercuric sulfate and sulfuric acid. Under these conditions mercuric iodide was first precipitated, but dissolved upon the addition of more mercuric sulfate. A fine white precipitate that separated was known to contain mercuric iodate bound in a complex compound.

Table III

The Effect of Sulfuric Acid and Mercuric Sulfate upon the Oxidation–Reduction Potential of Equivalent Mixtures of Iodine and Iodide at 25°

	Potential, pt. *vs.* satd. calomel, v.		
H_2SO_4 *N*	1 Soln. approx. 0.01 *N* in I_2 and KI	2 Soln. as in 1 plus 2 g. $HgSO_4$ per 50 ml.	3 As in 2 plus 2. g. $HgSO_4$
0.0	0.404	0.939	0.937
1.0	.404	.971	.966
2.0	.397	.980	.977
4.0	.379	.994	.996
6.0	.351	1.008	1.006

In this case it is evident that a reaction has occurred that has produced a system of very high potential (*iodate–iodide* system). The values are somewhat higher than the normal potential of the iodate–iodide–acid system because iodide ions are bound in the form of undissociated or complex substances. A mixture of mercuric sulfate, potassium iodide, potassium iodate and sulfuric acid of composition within the range of the measurements gave a potential in the measured range.

Foerster and Pressprich[16] have shown that arsenate–arsenite mixtures approach equilibrium potentials slowly and that a small quantity of iodide hastens the process. They observed that the iodine–iodide potential did not interfere with the measurements as long as the amount of this system added was equivalent to less than 10% of the arsenate–arsenite system. In our measurements a very minute crystal of potassium iodide was added to each solution so that the ratio of the two forms of arsenic was practically 1:1 at 0.01 *N* for each form.

Table IV

The Effect of Acidity upon the Oxidation–Reduction Potential of the Arsenate–Arsenite System, at 25°

Medium	E. m. f. Pt. *vs* satd. calomel electrode, v.
$NaHCO_3$ *p*H 7	0.06–0.08 Unsteady
Buffer, *p*H 5	.23–0.24 Unsteady
Buffer, *p*H 3	.28
N HCl	.334
2 *N* HCl	.358
3 *N* HCl	.382
4 *N* HCl	.400
6 *N* HCl	.446

(In Fig. 1, curve 2, 0.246 volt has been added to these values)

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(17) Kolthoff and Furman, "Potentiometric Titrations," 2d ed., John Wiley & Sons, Inc., New York, 1931, p. 71 ff.

(18) Furman and Wilson, This Journal, **50**, 288 (1928).

Discussion

The graphs (1, 2, Fig. 1) for the arsenic and iodine systems represent the oxidizing power of equivalent mixtures of the two forms in each case. At the beginning of the titration of a solution 0.01 N in arsenite and 1–2 N hydrochloric acid, the arsenate–arsenite ratio would be small and the potential would lie about 0.0885 volt below curve 2, while the potential of an iodine–iodide system, formed by the momentary *liberation of iodine* by interaction of iodate and the small amount of iodide derived from the iodate that had been added up to this point, would lie 2 or 3 times 0.059 volt above curve 1, Fig. 1. The iodine would be immediately reduced by the arsenite. This simple explanation in terms of oxidation–reduction potentials seems to account more adequately for the non-appearance of iodine in the early stages of such a titration than the qualitative interpretation in terms of relative reaction rates that were given by Schoonover and Furman.[12] In the latter a slow rate was attributed to the interaction of iodate, iodide and acid. As the titration proceeds, the relative positions of the two systems on the potential scale are reversed, and there is a sharp equivalence point corresponding to the oxidation of arsenite to arsenate and the reduction of iodate to iodine.

Figure 1 also indicates that the iodine–iodide system with mercuric chloride added is above the arsenate–arsenite system over the range of acidity that was studied. An increase in the concentration of mercury tends to bind the iodide more completely and the potential of a 1:1 mixture is raised still further by the increase.

The considerations that have been presented indicate clearly that new applications of iodine as an oxidizing agent may be made if mercuric chloride is added to the acidified solution that is to be titrated. Hitherto iodine has been used to titrate only the more powerful reductants such as stannous tin in acid solution. The latter may be titrated with iodate, which is reduced to iodide.[19] The steadiness of potentials at the end-points indicates that the presence of mercuric chloride tends to eliminate the troublesome autoxidation of iodide by air, which is catalyzed by many ions.

The potentials measured for the iodine–iodide system in the presence of mercuric sulfate and sulfuric acid are very much higher than for mixtures containing comparable amounts of mercuric chloride and hydrochloric acid. In contrast with the latter, doubling of the quantity of mercuric sulfate had practically no effect upon the potential. The iodine color disappeared in the sulfate case, and both electrical and chemical evidence points to the formation of iodate and iodide. It is difficult to make use of this high potential for titration purposes because of the appearance of insoluble products containing iodate.

The Iodometric Determination of Arsenic and Antimony in Acid Solution in the Presence of Mercuric Chloride

The preceding sections have indicated that the determination of trivalent arsenic or antimony may be made with standard iodine in a new range of acidity if mercuric chloride is added. The obvious advantages are the elimination of buffer mixtures and the possibility of operating in the presence of substances which would give undesirable precipitates or undergo oxidation at the pH which prevails in the usual iodometric method. It is necessary to use an excess of mercuric chloride that is sufficient to bind both the iodide introduced as potassium iodide in the standard solution and that which is formed by reduction of iodine.

The end-points of the oxidations may be determined either potentiometrically or with the aid of a suitable organic solvent for iodine, like carbon tetrachloride. The interference of mercuric chloride with the starch–iodide indicator for iodine is well known, and is probably to be attributed to binding of iodide and iodine by mercuric ion.[20] Mylius[21] proved that an iodide concentration of at least 10^{-6} g. is necessary. If an excess of potassium iodide is added, mercuric salts no longer interfere.[22] The early explanation by Millon[23] that mercuric chloride caused iodine to rearrange to iodine monochloride and iodide appears untenable because iodine may be extracted by carbon tetrachloride from solutions which fail to develop the color with starch.

Titration of Known Solutions.—Solutions of arsenite and antimonite were titrated with standard iodine solution in bicarbonate medium using starch as indicator. The titrations were repeated in solutions of various acidities with mercuric chloride present. In the latter case excel-

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[19] Ramsey and Blann, THIS JOURNAL, **56**, 815 (1934).

[20] Kolthoff, "Volumetric Analysis," Vol. II, J. Wiley & Sons, Inc., New York, 1929, p. 350.

[21] Mylius, *Ber.*, **28**, 388 (1896).

[22] Mahr, *Z. anal. Chem.*, **104**, 241 (1936).

[23] Millon, *Ann. chim. phys.*, **18**, 389 (1846).

lent agreement was obtained between potentiometric methods and the appearance of a permanent iodine color in a layer of carbon tetrachloride.

TABLE V

COMPARISON OF THE DETERMINATION OF ARSENIC AND ANTIMONY BY IODINE IN BICARBONATE MEDIUM WITH THAT IN MERCURIC CHLORIDE–ACID MEDIUM

Solution usd (As or Sb) ml.	Standard iodine required In $NaHCO_3$ medium, av. ml.	Standard iodine required In $HgCl_2$ acid medium, ml.	$HgCl_2$ soln., ml.	HCl concn., *N*
		A. Arsenic		
10.00	11.09	11.08	25	2.9
10.00	11.09	[a]	25	5.0
10.00	11.09	11.12	25	3.8
10.00	11.09	[a]	25	4.4
24.96	27.68	27.67	25	3.0
20.00	22.18	22.15	20	3.0
34.96	38.77	38.73	50	2.6
		B. Antimony		
10.00	13.40	13.40	25	2.7
10.00	13.40	[a]	25	4.2
24.96	33.37	33.40	50	2.6
24.96	33.37	33.32	50	3.0[a]
20.00	26.80	26.70	25	2.8

[a] Indicates that the reaction was too slow to be practical at the acidity in question.

There are several factors which determine the range of acid concentration that is permissible. At low acidities mercuric iodide tends to precipitate, and at high acidities the rate of reaction diminishes. At high acidities the potentials of the two systems tend to converge. The best condition is the lowest acidity that prevents the precipitation of mercuric iodide. An increase in the amount of mercuric chloride often permits the use of less acid.

The range of acidity is more restricted for antimony than for arsenic. The oxidation–reduction potential of the antimony system lies higher throughout the range than that of the arsenic system although exact data are not available. Latimer and Hildebrand[24] give 0.75 volt as the E_0 value for the antimony system.

If carbon tetrachloride is used as an indicating medium the mixture must be stirred quite vigorously as there is a tendency for iodine to accumulate in this solvent prior to the end-point. In the potentiometric titration there is no tendency for the potential to drift to lower values at the end-point after violent stirring for several minutes.

Applications.—The new method was further tested upon weighed samples of pure arsenious oxide. End-points were found with good concordance both potentiometrically[18] and with carbon tetrachloride. The solutions contained 50 ml. of saturated mercuric chloride solution and were 1.2–1.7 *N* in hydrochloric acid.

	1	2	3	4
As_2O_3 present, g.	0.0453	0.0739	0.0697	0.1203
As_2O_3 found, g.	$.0453_5$	.0740	.0696	.1202

Substances of antimony content unknown to the operator (M) were examined. Weighed samples of tartar emetic were dissolved in 20 ml. of water and 50 ml. of *N* hydrochloric acid saturated with mercuric chloride. Found: 37.48, 37.52 and 37.57% Sb. Value established by other investigators and other methods, av. 37.54% Sb.

One-gram samples of an alloy were dissolved in sulfuric acid (10 ml. concn.) with the usual precautions to remove sulfur dioxide and to prevent oxidation by air. After addition of 2 g. of sodium and potassium tartrate and 10 ml. of concd. hydrochloric acid and 50 ml. of the mercuric chloride, and proper dilution, potentiometric titrations were made. Found: 7.29 and 7.27% Sb, Bureau of Standards Certificate value 7.31% Sb. Owing to the presence of copper and other ions the use of carbon tetrachloride is not recommended for indication in the analysis of antimony alloys.

THE DETERMINATION OF ANTIMONY WITH STANDARD POTASSIUM IODATE

Introduction

Potassium iodate was first used by Andrews[25] for the determination of trivalent antimony, and the application of the method was extended by Jamieson.[26] The conditions employed were concentrated hydrochloric acid medium 4–6 *N*, in which the iodate is reduced to iodine monochloride. Lang[27] also used potassium iodate for the determination of antimony, but under conditions that result in the formation of iodine cyanide in a solution 1.2 *N* in hydrochloric acid; this method has the advantage that starch indicator may be used.

In the present investigation the reaction between antimonite and iodate has been studied with the object of testing the various stoichiometric processes that are possible, particularly at low acidities, with or without the addition of mercuric chloride.

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(24) Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, 1934, Appendix II.

(25) Andrews, THIS JOURNAL, **25**, 756 (1903).

(26) Jamieson, *Ind. Eng. Chem.*, **3**, 250 (1911).

(27) Lang, *Z. anorg. allgem. Chem.*, **142**, 242 (1925).

The Effect of the Concentration of Hydrochloric Acid upon the Stoichiometry of the Reaction between Antimonite and Iodate.—The acidity is the important factor in determining the stoichiometry of this reaction, as was observed by Schoonover and Furman[12] in the analogous reaction between arsenite and iodate. At a low range of acidities a definite equivalence point was detected corresponding to the reduction of iodate to iodine

$$5H_3SbO_3 + 2KIO_3 + 2HCl = I_2 + 5H_3SbO_4 + 2KCl + H_2O \quad (15)$$

In the absence of tartrates this "iodine" end-point is obtained over the narrow range of 2.4–3.5 *N* acid; with tartrates present the acidity may be as low as 1 *N*. Theoretically it might be possible to realize the stoichiometry of reaction (15) at somewhat higher acidities. The change in potential at the end-point would depend upon a transition from the iodine–iodide level to the iodine–iodine monochloride level which is less favorable for observation than a change to the iodine–iodate level.

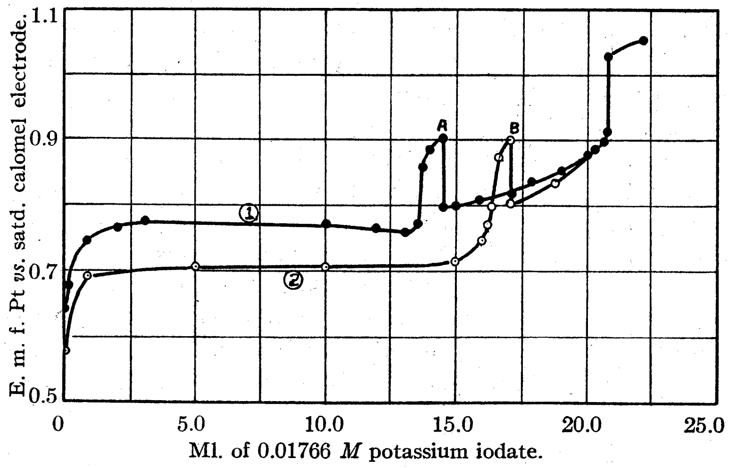

Fig. 2.—Curve 1: Graph of e. m. f. during titration of 0.0889 g. of antimony with 0.01766 *M* KIO_3 in the presence of mercuric chloride. Initial HCl concentration 2.7 *N*. At point A, HCl is added to bring its concentration above 5 *N*. Curve 2: repetition of titration as given in 1, with no mercuric chloride present.

The change in potential at the latter transition is only of the order of 0.03–0.07 volt per 0.05 ml. of 0.1 *N* potassium iodate. The classical potentiometric method rather than simplified methods was used for this small change. At acidities of 4–6 *N* the iodine that is liberated in the first reaction (15) is oxidized to iodine monochloride

$$2I_2 + KIO_3 + 6HCl = 5ICl + KCl + 3H_2O \quad (16)$$

and a second end-point is realized by adding hydrochloric acid and titrating to a second break in potential. The addition of the acid produces a drop in potential point B, curve 2, Fig. 2. At the latter end-point 0.05 ml. of 0.1 *N* iodate produces a rise of 0.07–0.12 volt. The presence of tartrate does not interfere with the detection of either end-point.

It was observed[12] that the presence of an immiscible organic solvent for iodine increases the potential change at the iodine equivalence point. Benzene is more effective than carbon tetrachloride and is to be recommended if the iodine end-point alone is to be determined. If the iodine monochloride end-point is also to be found, carbon tetrachloride offers mechanical advantages: ease of stirring from its position below the aqueous layer, and prevention of loss of iodine by volatilization.

The potassium iodate was 0.01766 *M*. The normalities for the iodide, iodine or iodine monochloride end-points are, respectively, 6, 5 or 4 times the molarity.

The iodine end-point was also obtained by titrating antimonite with iodate in sulfuric acid solutions from 2.7 to 6.0 *N*. In twelve determinations the maximum error was 0.2%. Only the iodine end-point is obtained in this medium.

The Oxidation of Trivalent Antimony in Hydrochloric Acid Solution with Mercuric Chloride Present.—In the presence of mercuric chloride there is a sharp end-point at the completion of the reduction of the iodate to iodide

$$3H_3SbO_3 + KIO_3 \xrightarrow[(HgCl_2)]{(HCl)} 3H_3SbO_4 + KI \quad (17)$$

TABLE VI

THE TITRATION OF ANTIMONITE WITH POTASSIUM IODATE IN HYDROCHLORIC ACID SOLUTIONS

Expt.[a]	Antimony present, g.	KIO_3 to iodine end-pt., ml.	Antimony found from 3, g.	KIO_3 to ICl end-pt., ml.	Antimony found from 5, g.	HCl concn. Init. *N*	HCl concn. Final *N*
2	0.0889	16.54	0.0889	20.70	0.0891	2.7	5.3
3	.0889	16.53	.0889	20.68	.0890	3.7	5.3
4	.0889	16.55	.0890	20.70	.0891	3.4	7.0
9	.0889	16.53	.0889	20.67	.0890	2.9	4.4
7[b]	.1555	28.81	.1549			1.4	
10[b]	.1779	33.31	.1781	41.43	.1782	0.8	4.7
25[b]	.0777	14.43	.0776	18.05	.0777	1.2	5.0

[a] The few experiments that have been selected include a fair sampling of the most and least accurate results of the whole series.

[b] Low initial acidity possible because tartrate was present.

We have explained the mechanism of this process on the basis of the formation of undissociated mercuric iodide which is soluble in hydrochloric acid. The iodine–iodide potential is so far increased by this process that iodine formed momentarily during the reaction is immediately reduced to iodide by the antimonite. The relative levels of the iodine and antimony systems under these conditions have been discussed (p. 158).

The first small increment of standard iodate beyond the iodide end-point produces free iodine which may be detected readily by extraction to a layer of carbon tetrachloride, and this simple visible indication agrees with the potentiometric end-point within about 0.02 ml. of 0.1 *N* solution. At acidities below 3.5 *N* the change in e. m. f. is of the order of 0.25 volt per 0.05 ml. of 0.1 *N* iodate at the end-point. The continuous-reading circuit was used for most of the determinations that are represented in Table VII. In many cases carbon tetrachloride was also present and a double indication was obtained. After the finding of this first end-point, increase of hydrochloric acid concentration to 4–6 *N* again causes a drop in potential (A, curve 1, Fig. 2) and the titration may be carried to the iodine monochloride point.

TABLE VII

THE DETERMINATION OF ANTIMONY WITH POTASSIUM IODATE IN THE PRESENCE OF MERCURIC CHLORIDE

1	2	3	4	5	6	HCl	
	Antimony present, g.	KIO_3 to iodide end-pt., ml.	Antimony found from 3, g.	KIO_3 to ICl end-pt., ml.	Antimony found from 5 g.	Concentration Init. N	Final N
Expt.[a]							
1	0.0889	13.80	0.0890	20.67	0.0889	2.6	5.3
2	.0889	13.79	.0890	no break		2.8	2.0
13	.1779	27.57	.1778	41.34	.1779	3.0	5.9
26	.1779	27.59	.1780	41.37	.1789	3.0	3.5
8[b]	.1555	24.05	.1552	36.06	.1551	1.8	4.0
15[b]	.0777	12.03	.0776	18.05	.0777	2.0	4.4
32[b]	.0889	13.78	.0889	20.67	.0889	1.4	3.8

[a] See notes below Table VI regarding selection of experiments, and normality of potassium iodate.

[b] Tartrates present.

Discussion

The general conclusions of these studies of the stoichiometry of the antimony reactions are similar to those in the investigation of the determination of arsenic;[12] the rather obvious conclusion that both arsenic and antimony if present together would be determined simultaneously according to any of the three possible reactions, has been verified by experiments which need not be detailed here.

The possibility of visual estimation of the iodide end-point has been pointed out; this applies to the determination of arsenic as well, although it was not noted in the former investigation.[12] We believe the mechanism of the oxidations by iodate in the presence of mercuric chloride to be essentially the same as those by iodine. The use of iodate rather than iodine offers the advantage of detecting the iodine monochloride end-point if the first end-point is overstepped.

Summary

1. The fact that the addition of iodine to solutions of mercuric salts in sulfuric, perchloric and nitric acids produces an immediate rearrangement into equivalent quantities of iodide and iodate has been confirmed.

2. The apparent failure of strong oxidizing agents to oxidize halides in the presence of highly ionized mercuric salts has been explained by showing that an oxidation does occur, but that the total oxidizing power of the solution toward a strong reducing agent like potassium iodide is preserved due to the autoxidation of the halogen under these conditions.

3. The effect of chlorides upon mixtures of bromate, iodide and mercuric nitrate has been observed, and the peculiar properties of solutions of iodine in mercuric chloride have been pointed out.

4. The ability to obtain the iodide equivalence point in the reaction between iodate and arsenite in the presence of mercuric chloride and hydrochloric acid has been attributed to an increase in the iodine–iodide potential due to the removal of iodide ions from solution as un-ionized mercuric iodide which is soluble in hydrochloric acid.

5. The oxidation–reduction potentials of equivalent mixtures of arsenate and arsenite and of iodine and iodide have been measured at various concentrations of hydrochloric and sulfuric acids. The very marked effect of mercuric chloride and mercuric sulfate upon the potentials of the iodine–iodide mixtures has been determined, and the increase has been attributed to binding of iodide by mercuric ions when chlorides are present and to the formation of iodate in the solutions containing sulfates.

6. It has been shown that a standard iodine solution may be used to titrate arsenite in solutions 1.2–3.8 *N* in hydrochloric acid, or antimonite in solutions 2–2.8 *N* in the acid, provided mercuric chloride is added to increase the iodine–iodide potential to a sufficient extent. This new

mode of titrations has been applied to the determination of arsenic and antimony in a few of the materials that are encountered in practice.

7. It is possible to determine antimony with standard potassium iodate under conditions such that the iodate may be reduced, as desired, to iodide, iodine or iodine monochloride. The first and third, or the second and third of the possible stoichiometric processes may be realized to give two end-points in a single titration. The new procedures involving the reduction of iodate to iodine at low acidities, or to iodide at low acidities in the presence of mercuric chloride, give results which compare favorably in accuracy with those obtained by other procedures.

PRINCETON, N. J. RECEIVED JULY 31, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Use of Iodine and of Potassium Iodate as Volumetric Oxidizing Agents in Solutions Containing Mercuric Salts. II. The Oxidation of Phenylhydrazine and of Semicarbazide by Means of Potassium Iodate

BY CLARK O. MILLER AND N. HOWELL FURMAN

Introduction

The nature and proportions of the end-products of the oxidation of hydrazine and its derivatives vary with the specific nature and the oxidation–reduction potential of the oxidizing system and with the *p*H of the medium. These facts have been established by various investigators.[1] It is a striking fact that hydrazine is oxidized quantitatively to nitrogen and water only by iodine, bromine or certain halogen oxyacids or salts;[1a,c] in other cases variable amounts of hydrazoic acid and ammonium salts are formed.

The determination with iodine must be made in buffered neutral or alkaline solutions since the reaction is too slow in acid medium for direct titrations. Hydrazine and its derivatives, especially phenylhydrazine, are readily oxidized by air under these conditions and hence the iodine method is of limited applicability.

We have shown[2] that the addition of mercuric chloride to the acidified solution that is to be titrated makes it possible to realize the stoichiometry of the reduction of iodate to iodide or of iodine to iodide smoothly in a range of acidity that would not be possible in the absence of the mercuric salt. This development increases the scope of iodine and iodate methods. We have chosen the oxidation of phenylhydrazine and of semicarbazide, respectively, as further illustrations of the application of potassium iodate under the new conditions of titration.

Phenylhydrazine.—Emil Fischer[3] stated that an emulsion of phenylhydrazine and water reacted as follows with iodine

$$2C_6H_5NHNH_2 + 2I_2 = 3HI + C_6H_5NH_2{\cdot}HI + C_6H_5N_3 \quad (1)$$

If an excess of hydrazine is used (2 moles per mole of $C_6H_5NHNH_2$) the reaction that occurs is

$$C_6H_5NHNH_2 + 2I_2 = 3HI + C_6H_5I + N_2 \quad (2)$$

according to von Meyer.[4] A volumetric process was based upon reaction (2) by adding a measured excess of standard iodine to the slightly alkaline solution, followed by back-titration with standard thiosulfate.

Fehling's solution oxidizes phenylhydrazine to nitrogen, water and benzene, and the nitrometric method of Watson Smith[5] is based on this reaction.

Seide, Scherlin and Bras[6] state that iodic acid reacts with phenylhydrazine in benzene–water emulsion to give a 25% yield of monoiodobenzene. Rimini[7] noted that hydrazine was oxidized by iodic acid, and Kurtenacker and Kubina[8] stated that direct titration of phenylhydrazine and semicarbazide with iodate to the iodine monochloride end-point is possible, but gave experimental evidence only for the latter compound. They also studied the determination of both substances with standard potassium bromate.

Mechanism of the Oxidation.—In our studies, two observations were made which do not seem in

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[1] (a) Browne and Shetterly, THIS JOURNAL, **30**, 53 (1908); (b) Hale and Redfield, *ibid.*, **33**, 1353 (1911); (c) Bray and Cuy, *ibid.*, **46**, 858 (1924).

[2] Furman and Miller, *ibid.*, **59**, 152 (1937).

[3] Fischer, *Ber.*, **10**, 1335 (1887).

[4] E. von Meyer, *J. prakt. Chem.*, **36**, 115 (1887).

[5] Watson Smith, *Chem. News*, **93**, 83 (1906).

[6] Seide, Scherlin and Bras, *J. prakt. Chem.*, **138**, 225 (1933).

[7] Rimini, *Gazz. chim. ital.*, **35**, I, 267 (1905).

[8] Kurtenacker and Kubina, *Z. anal. Chem.*, **64**, 388 (1924).

accord with the equation of von Meyer.[4] First, no liberation of nitrogen was observed in the early stages of the reaction, and second, no monoiodobenzene was detected. Nitrogen was evolved slowly toward the end of the titration. Upon treatment of the partially oxidized solution with alkaline beta-naphthol, a red dye was formed, indicating the presence of a diazonium salt. Equations for the three types of iodate processes may then be written:

(a) In 1–3 *N* HCl with mercuric chloride present

$$3C_6H_5NHNH_2 + 2KIO_3 + 3HCl = 3C_6H_5NNCL + \underset{\underset{HgI_2}{\downarrow}}{2KI} + 6H_2O \quad (3)$$

(b) In 1–3 N HCl

$$5C_6H_5NHNH_2 + 4KIO_3 + 9HCl = 5C_6H_5NNCl + 2I_2 + 12H_2O \quad (4)$$

(c) In 4–6 *N* HCl

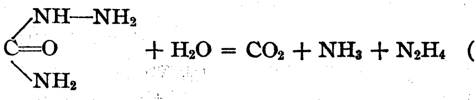
$$C_6H_5NHNH_2 + KIO_3 + 3HCl = C_6H_5NNCl + ICl + KCl + 3H_2O \quad (5)$$

The quantitative oxidation appears to be concerned with the formation of the diazonium salt, and the reaction of the latter with the medium to give nitrogen and phenol is a secondary process. The presence of phenol was confirmed by evaporating the solution to a small volume and coupling with phthalic anhydride.

The formation of the diazonium salt was also observed when phenylhydrazine was titrated with iodine. If a large excess of iodine–potassium iodide solution were used, both phenol and iodobenzene probably would be formed.

Chattaway[9] has shown that primary aromatic amines are transformed into diazonium salts by the action of other halogens (Cl_2 or Br_2) in glacial acetic acid solution.

Semicarbazide.—Prior studies of the determination of semicarbazide have been along the same lines as in the case of hydrazine. It was shown by Maselli[10] that semicarbazide is hydrolyzed with the formation of hydrazine by boiling in dilute sulfuric acid solution



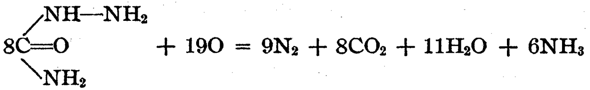
$$C{=}O\begin{smallmatrix}\diagup NH{-}NH_2\\ \diagdown NH_2\end{smallmatrix} + H_2O = CO_2 + NH_3 + N_2H_4 \quad (6)$$

The general concept that the hydrolysis of the compound must precede its oxidation apparently persists.[11]

Kurtenacker and Kubina[8] suggested two procedures for the determination of semicarbazide with potassium iodate. One consisted in adding a measured excess of standard potassium iodate, boiling to expel iodine and back-titration of the excess of the iodate. The other method was the conventional direct titration to the iodine monochloride end-point; few test analyses were given.

Hovorka[12] devised an indirect procedure for the determination of semicarbazide, using mercuric perchlorate and iodate. Thirty minutes are usually required for the oxidation to reach completion, after which the excess of iodate is determined by adding an excess of potassium iodide and titrating the iodine with standard thiosulfate solution. The chief advantage that this method offers is that the necessity of boiling iodine out of the solution is eliminated.

The oxidation of semicarbazide with either chlorate, bromate or iodate was investigated by Datta and Choudhury[13,14] with the object of developing a gasometric method for estimating the compound. The equation that was given for the reaction is

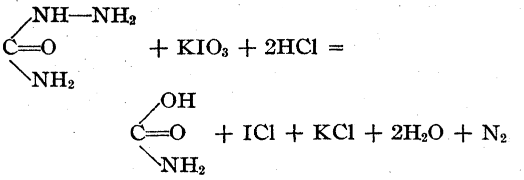


$$8C{=}O\begin{smallmatrix}\diagup NH{-}NH_2\\ \diagdown NH_2\end{smallmatrix} + 19O = 9N_2 + 8CO_2 + 11H_2O + 6NH_3 \quad (7)$$

The results deviate as much as 3.0% from the theoretical. The carbon dioxide must be absorbed. The fact that a functional group, $-NH_2$, is partially oxidized seems to make this type of procedure uncertain.

Bartlett[15] reported that 99.9% of the semicarbazide present was oxidized by excess of iodine in three seconds in a phosphate buffer of *p*H 7.

From a consideration of the various facts, the rapid reaction of semicarbazide with iodine in neutral solution or with iodate in acid solution is not due to hydrolysis, but depends upon direct attack of the hydrazine group with intermediate formation of unstable carbamic acid, which immediately breaks down to give carbon dioxide and ammonia



$$C{=}O\begin{smallmatrix}\diagup NH{-}NH_2\\ \diagdown NH_2\end{smallmatrix} + KIO_3 + 2HCl = C{=}O\begin{smallmatrix}\diagup OH\\ \diagdown NH_2\end{smallmatrix} + ICl + KCl + 2H_2O + N_2 \quad (8)$$

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(9) Chattaway, *J. Chem. Soc.* (London), **93**, 852 (1908).

(10) Maselli, *Gazz. chim. ital.*, **35**, I, 267 (1905).

(11) V. Harlay, *J. Pharm. Chem.*, **128**, 199 (1936); through *C. A.*, **30**, 4789 (1936). The first step of the method here proposed is the heating of the semicarbazide with 10, 20 or 30% hydrochloric acid in a sealed tube to hydrolyze it, after which the conventional iodometric titration is used.

(12) Hovorka, *Coll. Czechoslov. Chem. Commun.*, **3**, 285 (1931).

(13) Datta, THIS JOURNAL, **36**, 1014 (1914).

(14) Datta and Choudhury, *ibid.*, **38**, 2736 (1916).

(15) Bartlett, *ibid.*, **54**, 2853 (1932).

In solutions that are lower than 3 N in hydrochloric acid the iodate is reduced to iodine if mercuric salt is absent, or to iodide if mercuric chloride is present in concentration sufficient to bind the iodide. The latter stoichiometry has not been realized hitherto in a direct titration.

Experimental

Since the researches of Ardagh, *et al.*[16] have shown that solutions of phenylhydrazine are relatively unstable, even when acidified, and must be preserved under an inert atmosphere, it was found desirable in our work to weigh samples of purified phenylhydrazine hydrochloride for each experiment. Samples of an Eastman product were recrystallized from hot water after decolorizing them with charcoal. The crystals were washed thoroughly with alcohol, then with ether and were dried by vacuum desiccation overnight. Drying for short intervals at 100° is also permissible, but at higher temperatures discoloration occurs and partial rearrangement to *p*-phenylenediamine takes place.

The purity of the crystals was tested by titration of samples with sodium hydroxide that had been standardized against pure benzoic acid, using phenolphthalein indicator. At the equivalence point the solution contains sodium chloride and free phenylhydrazine, $K_b = 1.6 \times 10^{-9}$. Hence for solutions between 0.1 and 0.01 N the *p*H at the end-point is from 9.1–8.6. In a series of nine titrations the maximum error was ±0.25% and the average was +0.03%, on the assumption of a pure product.

The standard potassium iodate and the mercuric chloride solutions were prepared as in the preceding investigation,[2] where the nature of the electrical apparatus is also mentioned.

Semicarbazide hydrochloride, from the G. F. Kahlbaum Co., was purified by dissolving in distilled water, filtering, and precipitating by the addition of 1–2 volumes of ethyl alcohol. The crystals were filtered, washed repeatedly with 95% alcohol, then with ether. After vacuum desiccation overnight the material was suitable for weighing. The tested technique of purification together with the titrations to the iodine monochloride point with iodate served to establish the purity of the material.

The Titration of Phenylhydrazine Hydrochloride with Standard Potassium Iodate in the Presence of Hg^{++}.—Portions of the purified substance ranging from 0.08 to 0.26 g. were titrated in solutions of various acidities as shown in Table I. In each case 15–25 ml. of saturated mercuric chloride was present, and the final volume after titration was about 150 ml. In neutral or feebly acid solution phenylhydrazine reduces mercuric ion; it is therefore desirable to acidify the solution before adding the phenylhydrazine. No reduction occurred when the acidity was at least 2 N. If only a small amount of mercurous chloride is formed, the solution need not be discarded because the iodate oxidizes the mercurous chloride to mercuric, during the titration.

At the end of the titration to the first end-point (iodide) the potential jump is 0.06 to 0.08 volt per 0.05 ml. of 0.1 N KIO_3; either classical or simplified methods may be used. The use of carbon tetrachloride for the "iodide" end-point is not very satisfactory.

TABLE I

POTENTIOMETRIC TITRATION OF PHENYLHYDRAZINE WITH POTASSIUM IODATE SOLUTION IN THE PRESENCE OF MERCURIC CHLORIDE

1 Sample, g.	2 KIO_3 to iodide end-pt., ml.	3 $C_6H_5N_2H_3HCl$ found from 2, g.	4 KIO_3 to ICl end-pt., ml.	5 Subst. found from 4	6 Concentration of HCl, N	7
					Init.	Final
0.1831	35.55	0.1833	53.30	0.1832	1.1	3.6
.1119	21.73	.1120	32.53	.1118	2.8	4.0
.1447	28.05	.1446	42.05	.1446	2.6	4.2
.1328	25.70	.1325	38.59	.1326	2.8	3.9
.1590	30.77	.1587	46.08	.1584	1.6	5.0
.1099*	21.28	.1098	32.05	.1101	3.2	4.1
.1219*	23.63	.1218	35.50	.1220	3.6	4.2
.1159*	22.45	.1158	33.66	.1157	2.4	3.9

The KIO_3 solution was 0.02378 M and the normality is, respectively, 6 or 4 times molarity for the iodide and iodine monochloride end-points. In the last three determinations, marked (*), from 0.5 to 1 ml. of aniline was present.

After finding the first end-point, the stoichiometry of equation (5) may be realized by continuing the titration after adding hydrochloric acid to 4–6 M concentration. Potential break: 0.12–0.16 volt per 0.05 ml. of 0.1 N KIO_3. Care must be taken to avoid the accumulation of nitrogen bubbles on the platinum indicator electrode.

It is of interest that potassium iodate oxidizes the hydrazine group selectively in the presence of an aromatic amine (aniline), whereas more powerful oxidants attack the latter under similar conditions.

A series of eight determinations under conditions similar to those indicated in Table I, but with omission of the mercuric salt, proved that it was possible to realize the stoichiometry of equation (4); after adding hydrochloric acid to 4–6 M concentration the titration may be continued to a second end-point corresponding to equation (5). The maximum errors were +0.20 and −0.30%. Only three determinations were in error by more than 0.2%.

A critical experimental study of the conventional iodine method yielded the following conclusions: low results are obtained in alkaline solution; the reaction is incomplete in strongly acid solution; correct results are obtained when the *p*H of the solution is between 2 and 5. We found the iodine method to be tedious due to the sluggishness of the reaction near the end-point. We regard the various iodate procedures that have been described as far superior to the titration with iodine.

The Oxidation of Semicarbazide in the Presence of Mercuric Chloride.—The weighed samples were dissolved in water and hydrochloric acid (see Table II) and 15–30 ml. of saturated mercuric chloride solution was added. The initial volume ranged from 40–80 ml. The progress of the reaction was followed potentiometrically or by noting the readings of a sensitive galvanometer in series with a high resistance. The reaction is slow near the "iodide" end-point, so that the last 0.2 ml. of reagent must be added in drops at about thirty-second intervals. Each drop produces a potential rise which diminishes rapidly prior to the end-point, but does not diminish at the end-point; change, 0.08 volt per 0.05 ml. of 0.1 N KIO_3. Up to a certain limit the addition of more mercuric chloride makes the process more rapid.

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[16] Ardagh, *et al.*, THIS JOURNAL, **54**, 721 (1932).

The iodine monochloride equivalence point is very sharp and must be recommended as the most satisfactory for ordinary titrations. If a carbon tetrachloride layer is used for indication, very thorough stirring or shaking is necessary near the end-point. The break in e. m. f. is about 0.13 volt per 0.05 ml. of 0.1 N reagent. The data in Table II are fairly representative of 22 determinations that were made.

TABLE II

POTENTIOMETRIC TITRATION OF SEMICARBAZIDE HYDROCHLORIDE WITH STANDARD POTASSIUM IODATE IN THE PRESENCE OF MERCURIC CHLORIDE

1	2	3	4	5	6	7
Sample, g.	KIO_3 to "iodide" end-pt., ml.	Subst. found from 2 g.	KIO_3 to ICl end-point, g.	Subst. found from 4 g.	Concn. of HCl, N	
					Initial	Final
0.1263	31.80	0.1264	47.50	0.1266	1.1	6.1
.1026	25.76	.1025	38.68	.1026	0.8	3.7
.1362	34.73	.1362	52.04	.1361	.8	3.4
.1514	38.48	.1509	57.84	.1514	1.7	4.3
.0627	15.95	.0626	24.00	.0627	1.3	5.0
.1070	27.20	.1066	40.82	.1067	1.2	4.0
.0874*			33.42	.0874		4.65
.1612*			61.70	.1613		4.3
.1055			40.40	.1058		4.8

The potassium iodate solution was 0.02378 M for the first two determinations and 0.02344 for the others. The normalities for the iodide and iodine monochloride reactions are, respectively, 6 and 4 times the molarity. In the determinations marked (*) the solution contained 0.1 to 0.5 g. of urea. Potassium iodate oxidizes the aliphatic hydrazine derivative selectively in presence of the corresponding amino compound just as was the case with the aromatic substances.

A number of experiments proved that it was impractical to base a direct titration on the process involving the reduction of the iodate to iodine in dilute hydrochloric acid solution (less than 3 N) in the absence of mercuric chloride. The reaction was extremely slow in the neighborhood of the end-point.

Of the determinations made to the iodine monochloride point only four deviated as much as 0.21–0.27% from the theoretical value, and the average deviation was −0.05%. Semicarbazide could therefore serve as a standard substance since it is purified and preserved easily. The substance has suitable characteristics for the removal of an excess of an oxidizing agent that is not powerful enough to attack the amino group. The nature of the products (CO_2, N_2, ammonium salt and water) is favorable for such application.

Summary

1. The oxidation of phenylhydrazine in acidic solution by potassium iodate or by iodine has been shown to result in the formation of the diazonium salt which slowly hydrolyzes giving off nitrogen and forming phenol in the absence of an excess of potassium iodide.

2. The iodate procedures have been compared with the iodine method and they offer decided advantages of rapidity and ease of execution.

3. Potassium iodate does not attack aniline readily in cold acidified solutions and correct results are obtained for phenylhydrazine in the presence of the former.

4. The optimum conditions for the stoichiometric reduction of iodate to iodide, with mercury present, or to iodine monochloride in 3–6 N hydrochloric acid solution by both phenylhydrazine and semicarbazide have been investigated. In the case of phenylhydrazine it was also found possible to obtain an end-point corresponding to the reduction of the iodate to iodine, at low acid concentration.

5. The mechanism of the oxidation of semicarbazide has been considered and it has been pointed out that hydrolysis need not precede the oxidation process.

6. Potassium iodate attacks urea very slowly in cold acidified solutions and semicarbazide may therefore be titrated selectively in the presence of the former substance.

PRINCETON, N. J. RECEIVED AUGUST 20, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of Gaseous Addition of Halogen Acids to Isobutene

BY G. B. KISTIAKOWSKY AND C. H. STAUFFER

In a recent paper[1] the thermal decomposition of tertiary butyl chloride into hydrogen chloride and isobutene has been shown to be a clean gaseous unimolecular reaction. The present communication deals with some measurements of the tertiary butyl bromide decomposition, and with the study of the reverse reactions. These latter are of considerable interest because work on liquid phase reactions of this type has led to the discovery of peculiar effects, due supposedly to the presence of oxygen or peroxides,[2] and because Maass[3] has claimed that a discontinuity in reaction rates exists in the transition from the liquid to the gaseous state which cannot be explained by the concentration effect alone.

Equilibrium between halogen acids and olefinic hydrocarbons in the gaseous state has been investigated in the past infrequently. The work of Brunel[4] on isobutene and hydrogen bromide will be discussed later. Wibaut, Rutgers and Diekmann[5] reported an 84.4% yield of ethyl chloride at *ca.* 200° and atmospheric pressure, while Tilman[6] finds about 4% decomposition of ethyl chloride around 120°. These studies have been made with the aid of catalysts. While they possibly cannot be regarded as very accurate determination of equilibria, they indicate, as will be seen from comparison with the data here presented, that the free energies of formation of alkyl halides are not greatly dependent either on the alkyl or on the halogen constituent of the molecule.

The study of the decomposition of tertiary butyl bromide using technique developed earlier for the chloride presented no new difficulties, but repeated experiments made to study the addition of hydrogen chloride and bromide to ethylene, pentene-2 and isobutene[7] failed to discover any homogeneous reaction. This is in accord with the findings of Maass, but it does not mean that the gaseous kinetics of these reactions are in any way "abnormal." As will be seen later, the activation energies of the association reactions with isobutene are fairly high, causing slow rates at lower temperatures, while at higher temperatures the equilibria are too unfavorable for a study at and below atmospheric pressure.

It thus became necessary to determine their kinetics by combining rate expressions for the decomposition with equilibria data; the latter were obtained with the aid of catalyzed reactions. This procedure suffers, of course, from increased errors, but the over-all accuracy is sufficient, we believe, to draw the most essential conclusions.

Experimental

The decomposition of *t*-butyl bromide and the equilibrium composition in both reactions were studied in a static system by pressure measurements. For the decomposition experiments the system was the same as described previously;[1] it was used also for the equilibria studies, but in this case the containers of the halogen hydrides were separated from the reaction flask by a glass valve, whereas between the isobutene and the *t*-butyl halide containers and the flask were stopcocks followed by a glass valve. This latter communicated also, through a third stopcock, with the pumping system.

The same treatments of the flask, even perhaps somewhat more protracted, were necessary to obtain a homogeneous decomposition of *t*-butyl bromide as were described in the case of *t*-butyl chloride.

For the equilibria studies flasks of varying catalytic activity were used at the several temperatures studied. For the lowest temperature a one-liter flask filled with 100 g. of glass wool (soft glass) was prepared; the others were filled with broken glass (Pyrex) of about pea size and with pieces of 10-mm. tubing, while for the highest temperatures an empty flask was found to give the most convenient rates. The equilibrium was usually indicated by a complete cessation of pressure changes, but in some cases a very slow, steady decrease of pressure was observed, due, no doubt, to a polymerization reaction of the olefin. In these runs the equilibrium pressure was extrapolated to zero time assuming a constant rate of polymerization. The whole correction was small.

According to Brunel,[4] besides the *t*-butyl halide, considerable quantities of the isobutyl halide are formed at temperatures in the neighborhood of 270° (25% of isobutyl bromide), while at 100° their relative yield is negligible. If true, this finding would indicate that the heat of formation of the iso compound differs very considerably from that of the tertiary halide, while the free energies of their formation are nearly identical at 270°. Such a conclusion

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[1] Brearley, Kistiakowsky and Stauffer, THIS JOURNAL, **58**, 43 (1936).

[2] Kharasch and Hinckley, *ibid.*, **56**, 1243 (1934).

[3] Maass, *ibid.*, **46**, 2664 (1924); **47**, 2883 (1925).

[4] Brunel, *ibid.*, **39**, 1978 (1917).

[5] Wibaut, Diekmann and Rutgers, *Rec. trav. chim.*, **47**, 479 (1928).

[6] Tilman, Thesis, Amsterdam, 1928.

[7] Hydrogen bromide and isobutene have a barely measurable homogeneous rate at 300°. About 2% reaction occurs in six minutes with little further change.

is not very plausible and Brunel's measurements were repeated avoiding his most probable source of error, a reaction between condensed isobutene and hydrogen bromide. The method consisted in passing a metered mixture of hydrogen chloride and isobutene through a flask packed with glass wool and maintained at 270°. The contact time was more than amply sufficient to establish equilibrium. After leaving the furnace the gases passed through several bubblers containing a 7.5% solution of sodium bicarbonate, to remove hydrogen chloride, then a calcium chloride tube and a trap at 0° in which the alkyl chlorides were collected; another trap, at −80°, collected the unreacted isobutene. About 13 cc. of butyl chlorides was obtained. This was distilled through a 3-ft. (91 cm.) Podbielniak-type column with a 10:1 reflux ratio. Less than 0.5 cc. came over before 50.4° and the rest boiled at 50.6° until the pot was dry. The hold-up in the column amounted to 1.5 cc. It had a refractive index of $n^{20}{}_D$ 1.3901, while the distillate had a (uniform) refractive index of 1.3839. If this entire difference is attributed to the presence of isobutyl chloride in the residues, its concentration in the initial mixture is found to be 7.8%. Considering all probable errors, such as the higher volatility of *t*-butyl chloride, the presence of polymers, etc., the real concentration is probably smaller. This experiment could not be repeated with hydrogen bromide because of rapid hydrolysis of *t*-butyl bromide by the bicarbonate solution, but we believe that essentially the same conditions prevail in that system also. Brunel's finding is accountable by a reaction between hydrogen bromide and isobutene when these were condensed to a liquid, which would probably give, since oxygen was not carefully excluded, mainly isobutyl bromide. In his experiments at 100°, on the other hand, only a little free hydrogen bromide remained upon establishment of gaseous equilibrium and thus the liquid phase reaction was insignificant.

Preparation of the Materials.—The *t*-butyl bromide was obtained from Eastman Kodak Co. and was purified by a slow crystallization with stirring. When approximately half of the material was frozen, the crystals were separated from the liquid, and used for the kinetic experiments. No difference in results was observable between different samples. The *t*-butyl chloride was made as described previously.[1]

The isobutene was part of the material prepared in this Laboratory for the calorimetric study of its heat of hydrogenation[8] and was used without further purification.

Hydrogen chloride was prepared by dropping concd. C. P. sulfuric acid on sodium chloride and concd. hydrochloric acid solution. It was dried over sulfuric acid, liquefied and distilled once from trap to trap *in vacuo*. The middle third was used.

Hydrogen bromide was prepared by dropping bromine on naphthalene. The evolved gases were led over naphthalene and copper turnings, to remove unreacted bromine. Hydrogen bromide was liquefied and distilled from trap to trap once. The middle third was used.

Results and Interpretation.—A summary of the rate constants and the experimental data for the thermal decomposition of the tertiary butyl bromide will be found in Table I. Run 95p was carried out in a packed flask having ten times the surface volume ratio of the unpacked flask. The packed flask had been given nine treatments to deactivate the glass surface. Each treatment consisted in allowing about 200 mm. of *t*-butyl bromide to decompose in the flask at a temperature of 500° for from five to ten hours. The comparison indicates quite clearly the homogeneity of the reaction.

TABLE I

DECOMPOSITION OF *t*-BUTYL BROMIDE

Run	T, °K	P, mm.	$k \times 10^4$, sec.$^{-1}$
87	508.9	97	0.836
95p	509.9	101	1.07
88	510.2	96	1.01
84	526.1	93	3.41
82	540.5	101	9.40
85	559.3	95	32.5
90	562.5	48	40.0
83	562.7	95	42.0
86	564.8	95	44.0

In Tables II and III will be found the equilibrium constants for the chloride and bromide, respectively. Runs whose numbers include an (a) are those in which the equilibrium was approached from the side of addition, while the letter (d) refers to an approach through the decomposition reaction. Those containing (ad) refer to runs in which the tertiary bromide was first decomposed at a rate too rapid to get an accurate initial pressure, and then the reaction was forced back by introducing a measured amount of hydrogen bromide and following the pressure until the equilibrium was again established. The usual plot of the decomposition rate constant of the bromide gives a good straight line and leads to an activation energy of 40,500 ±

TABLE II

EQUILIBRIUM BETWEEN HYDROGEN CHLORIDE, ISOBUTENE AND *t*-BUTYL CHLORIDE

Run	T, °K.	$P_{\text{equil.}}$, mm.	K, atm.$^{-1}$
1d	361.3	263.5	284
2d	364.9	265.8	234
3d	368.0	280.0	194
4d	377.4	287.5	110
5d	380.4	290.8	92.0
6d	381.4	209.6	80.1
7d	415.0	228.9	14.1
8d	415.2	288.0	13.7
9d	421.3	340.6	10.6
10a	509.5	414.9	0.284
11a	510.4	484.6	.256

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(8) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 876 (1935).

TABLE III

EQUILIBRIUM BETWEEN HYDROGEN BROMIDE, ISOBUTENE AND *t*-BUTYL BROMIDE

Run	T, °K.	$P_{\text{equil.}}$, mm.	K, atm.$^{-1}$
12ad	375.0	297.7	440
13ad	380.8	278.8	385
14d	382.8	157.4	443
15ad	384.8	306.5	410
16d	386.3	190.0	332
17d	400.2	119.2	130
18d	401.7	117.7	142
19d	402.0	115.8	129
20d	405.9	116.6	118
21d	409.2	119.5	88.4
22d	410.3	132.3	97.5
23d	410.7	163.0	82.0
24d	426.0	133.9	37.4
25a	443.2	127.1	11.8
26a	445.9	132.6	9.94
27d	471.1	163.2	4.21
28d	473.6	161.2	4.14
29d	473.6	164.1	3.94
30d	475.6	226.9	3.25
31d	475.8	165.9	3.49
32d	477.8	228.1	3.07
33d	479.4	228.2	3.05
34a	482.9	251.5	2.45
35d	508.5	189.4	1.32
36a	514.2	303.8	0.724
37a	515.1	301.8	.821
38a	531.7	218.1	.438

1000 cal. Using this value, the expression for the rate constant can be cast into the form

$$\text{(Bromide) } k_{\text{d}} = 10^{13.3 \pm 0.4}\, e^{-(40,500 \pm 1000)/RT} \text{ sec.}^{-1}$$

To be compared with it is the expression for the decomposition of the chloride:[1]

$$\text{(Chloride) } k_{\text{d}} = 10^{13.9 \pm 0.7}\, e^{-(45,000 \pm 1900)/RT} \text{ sec.}^{-1}$$

It is apparent that while the activation energies of the two reactions are markedly different (see Fig. 1), the *A* factors, within experimental uncertainties, are identical. The lower activation energy of the bromide is in good accord with the lesser stability of this compound as is known from general chemical experience.

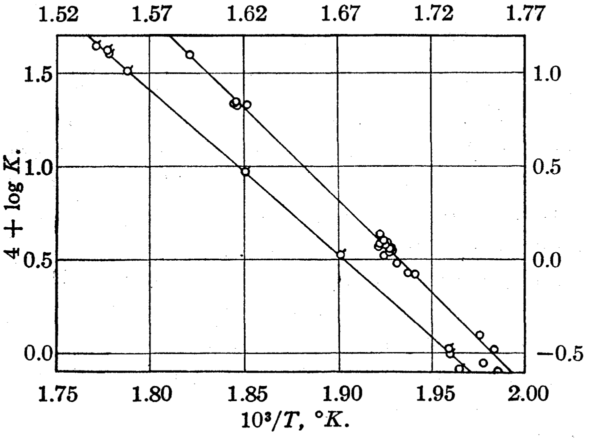

Fig. 1.—Plot of the reciprocal of the absolute temperature against the logarithm of the unimolecular rate constant. Upper curve refers to the decomposition of *t*-butyl chloride, and the lower curve to *t*-butyl bromide.

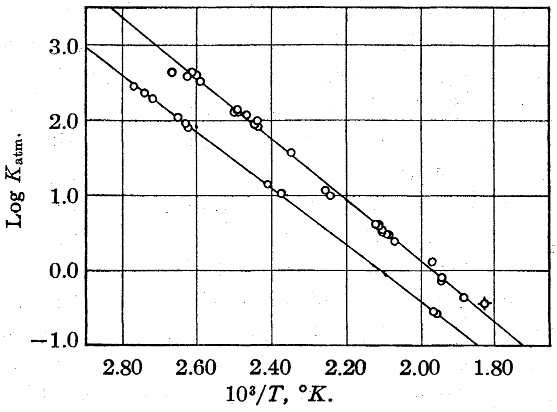

Fig. 2.—Plot of the reciprocal of the absolute temperature against the logarithm of the equilibrium constants expressed in atmospheres. The upper curve refers to the HBr, isobutane, and *t*-butyl bromide equilibrium, and the lower curve to the HCl, isobutane, and *t*-butyl chloride equilibrium. The crossed circle is a value found by Brunel.

The logarithmic plots of the two equilibrium constants will be found in Fig. 2 together with the values given by Brunel.[4] Both equilibria give good straight lines and the expressions for the constants can be cast into the forms

$$\text{(Chloride) } \log K = (17{,}100/4.58T) - 7.89$$
$$\Delta F^{\circ} = 17{,}100 + 36.1T \text{ (atmospheres standard)}$$

with an uncertainty of *ca.* 500 calories in the heat of reaction;

$$\text{(Bromide) } \log K = (18{,}900/4.58T) - 8.12$$
$$\Delta F^{\circ} = -18{,}900 + 37.2T$$

with an uncertainty of *ca.* 900 calories in the heat of reaction. The difference of the two heats of reaction exceeds the probable error, even when the uncertainty caused by the possible formation of isobutyl halides is included. As stated before, Brunel's finding of a large amount of iso compound at 270° could not be substantiated and a plausible explanation of his experimental data has been offered. A correction for 8% iso chloride found at 270° (and a negligible amount at low temperatures) would change the heat of reaction only by some 200 cal./mole and can thus be disregarded in the following calculations.

Changing the equilibrium constants to mole/cc.

as units, converting the heats of reactions to constant volume and utilizing the relation

$$K = k_{\text{ass.}}/k_{\text{dec.}}$$

the following expressions are obtained for the association rate constants

$$(\text{Chloride})\ k = 10^{11.0 \pm 1.0}\, e^{-(28{,}800 \pm 2400)/RT} \text{ cc./mole sec.}$$
$$(\text{Bromide})\ k = 10^{10.2 \pm 0.7}\, e^{-(22{,}500 \pm 1900)/RT} \text{ cc./mole sec.}$$

As before, the A factors can be considered as identical within experimental errors, while the activation energies are decidedly different. This difference is even more marked than in the decomposition reactions.

The A factors of these reactions are considerably smaller than the usual kinetic collision factors, but this is to be expected in association reactions of large molecules and the best method to investigate whether they are "normal" is to compare them to the theoretical expressions for the rates of such reactions, as developed recently in several publications. Use will be made of the Eyring[9] notation and concept of the activated complex but no attempt will be made to calculate the potential energy surface of the reaction. It will be assumed instead that the activated complex is identical in size and shape with the final molecule (*t*-butyl chloride), an assumption made by Rice and Gershinowitz[10] in their "exact orientation" theory. An estimate of the vibrational frequencies of the activated complex being uncertain, to say the least, these frequencies will be regarded as unknown and to be deduced from a comparison of the calculated and measured rate constants.

Two possibilities offer themselves for calculation. One may regard that CH_3 group, in the activated complex, which becomes $=CH_2$ group in isobutene as possessing free rotation. Then the activated complex is identical with *t*-butyl chloride in all degrees of freedom, but one, and the calculation conforms entirely to the "exact orientation" theory. Or, one may suppose that free rotation does not exist in the activated complex and that instead a torsional vibration (of low frequency) is present. The two methods of calculation lead to formally different equations. However, no decision is possible between them because numerically very similar results are obtained in both cases. This is due to the circumstance that the partition function of internal rotation of a CH_3 group (one degree of freedom) is almost equal numerically to the extra symmetry factor to be assigned to the activated complex when it is assumed to have free internal rotation of that group. If the activated complex has free rotation of all three (equivalent) methyl groups, its symmetry factor is taken at 3^4; if free rotation exists in only the non-reacting methyl groups, the factor is 3^2. The symmetry factor of the non-activated *t*-butyl chloride is 3^4, that of isobutene 18. The internal rotational partition function of CH_3 is calculated to be equal to 7.2 at 500°K. The other numerical data used are:

The product of the moments of inertia of isobutene is 6.6×10^{-115} g.^{3} cm.^{6}. The product of the moments of inertia of *t*-butyl chloride is 58×10^{-115} g.^{3} cm.^{6}. The moment of inertia of hydrogen chloride is 2.6×10^{-40} g. cm.^{2}. The former two have been calculated using Pauling's internuclear distances and tetrahedral angles. Using the internal free rotation model we find for the association reaction rate constant

$$k_{\text{ass.}} = 1.5 \times 10^9 \frac{F^*}{F_1 F_2} \frac{500}{T} e^{-(E_0 - RT)/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1} \quad (1)$$

The F's stand here for the vibrational partition functions, F^* containing three more of them than F_1 and F_2 together. The value before the exponential cannot be compared directly with the experimental figure because of differences in the activation energy. The following procedure which has been adopted to correct E_0 to the temperature of the experiments is not free from objections but it seems to us to be practically the most reasonable one. The rate constant for the decomposition reaction is calculated to

$$k_{\text{dec.}} = 2.8 \times 10^{13} \frac{F^*}{F_3} \frac{T}{500} e^{-(E_0 + RT)/RT} \text{ sec.}^{-1} \quad (2)$$

where F^* contains one less vibration than F_3. $E_0 + RT$ is the activation energy at the temperature of the experiments unless the vibrational heat capacities of the associated molecule and the activated complex are different. Comparing the numerical factor in (2) with the experimental values, one finds that they are practically identical for the *t*-bromide, while that of the *t*-chloride is about three times larger. This we are inclined to ascribe to experimental errors, in accord with the "exact orientation" theory which does not assume any loosening of the molecule on transition to the activated state and hence prescribes essentially identical vibrational partition functions for the reactant molecule and the activated

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(9) Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

(10) Rice and Gershinowitz, *ibid.*, **3**, 479 (1935).

complex. Because the equilibria data can be regarded as quite accurate, the experimental association rate A-factor of the chloride must also be reduced by a factor three to make everything self-consistent. The ratio of the experimental value to the above calculated one is then equal to about nine. Assuming now that the difference between E_0 and the experimental activation energy is due to the T factor in equation (1) and the contribution of the three extra vibrations in F^*, one finds by trial that a factor four for the product of the three extra vibrational partition functions in F^* gives the correct answer. Hence, the average frequency of the new vibrations in the activated complex is *ca.* 340 cm.$^{-1}$.

For the model of the activated complex, in which the CH_2 group of the butene has not acquired free rotation, one finds

$$k_{\text{ass.}} = 1.1 \times 10^9 \frac{F^*}{F_1F_2}\left(\frac{500}{T}\right)^{3/2} e^{-(E_0-{}^3/_2RT)/RT} \text{ cc. mole}^{-1}\text{ sec.}^{-1} \quad (3)$$

and

$$k_{\text{dec.}} = 2.2 \times 10^{13} \frac{F^*}{F^3}\left(\frac{T}{500}\right)^{1/2} e^{-(E_0+{}^1/_2RT)/RT} \text{ sec.}^{-1} \quad (4)$$

where F^* contains four more vibrations than F_1 and F_2 together and the same number as F_3. Proceeding much in the same manner as outlined before, one arrives at an average frequency of vibrations formed in the association reaction of about 450 cm.$^{-1}$. In view of the experimental errors and the many approximations made in calculations it is impossible to make a selection between these two sets of data. Both are quite reasonable although, as in the case of Diels–Alder association reactions,[11] somewhat higher frequencies would have been even more acceptable. In any case it should be clear from the preceding calculations that the association of halogen hydrides and isobutene in the gas phase proceeds according to entirely normal kinetics, calculable, in the order of magnitude at least, by the statistical theory of reaction rates. Some details of the calculations and some experimental data are not as perfect as could be desired but the main purpose of this investigation—a demonstration that the kinetics of these associations are "normal"—has been achieved. They cannot be observed directly merely because of coöperation of a high energy of activation and an unfavorable equilibrium. This applies *a fortiori* to the formation of secondary and primary halides because their energies of activation are probably still higher. This may be deduced tentatively from the generalization that the stability of primary and secondary halides is greater than that of the tertiary ones,[12] coupled with the not greatly different free energy change in the reaction.

Some remarks concerning association reactions of halogen acids and ethylenic hydrocarbons in liquid media are, perhaps, in order here. Present work leaves no doubt that these reactions at and near room temperature proceed via some mechanism quite different kinetically from the one here discussed. This is inevitable since, even allowing for concentration changes, one finds vanishingly small reaction rates at room temperature, with the expressions here given, whereas rapid rates have been observed in several widely different solvents.[2,5] This latter circumstance would make it very improbable that the fast rate is due to some specific effect of solvent on the activity of the reactants, or on that of the activated complex. Hence, the most plausible mechanism accounting for the reaction rate in liquids is a chain mechanism. In the light of such interpretation the findings of Kharasch,[2] on the action of oxygen, may find a reasonable explanation, although on the whole the effect is puzzling. In this connection it may be added also that in the gas phase reaction the addition of small amounts of oxygen does nothing but accelerate the wall reaction.

Summary

The rate of gaseous thermal decomposition of *t*-butyl bromide has been investigated in the temperature region of 509–564°K., and it was found to be a homogeneous unimolecular reaction.

The reaction rate constant was found to be

$$k = 10^{13.3 \pm 0.4}\, e^{-(40,500 \pm 1000)/RT} \text{ sec.}^{-1}$$

The equilibrium of *t*-butyl bromide and *t*-butyl chloride with isobutene and the respective halogen acid was investigated in the temperature region 361–533°K.

The heats of reaction at constant pressure for the associations were found to be −17,100 ± 500 cal., and −18,900 ± 900 cal. per mole for the formation of the chloride and the bromide, respectively.

The free energy changes of the reactions were found to be expressed in the form

(Chloride) $\Delta F^\circ = -17{,}100 + 36.1T$ (atmospheres standard)

(Bromide) $\Delta F^\circ = -18{,}900 + 37.2T$

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[11] Kistiakowsky and Lacher, THIS JOURNAL, **58**, 123 (1936).

[12] *Cf.* Vernon and Daniels, *ibid.*, **55**, 922 (1933).

The rate equations of the association reactions were calculated from these data and found to be:

$$(t\text{-Chloride})\quad k = 10^{11.0 \pm 1.0}\, e^{-(28{,}800 \pm 2400)/RT}$$
$$(t\text{-Bromide})\quad k = 10^{10.2 \pm 0.7}\, e^{-(22{,}500 \pm 1900)/RT}$$

The units are cc. moles^{-1} sec.$^{-1}$.

The isomerization of *t*-butyl chloride to isobutyl chloride at 270° was investigated, and found to be less than 7.8% at equilibrium.

The statistical mechanical explanation of slow reaction rates in the form developed by Eyring was applied, and reasonable agreement was found with the theory.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 2, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND THE DEPARTMENT OF HYGIENE AND BACTERIOLOGY, UNIVERSITY OF CHICAGO]

Some Chemical Properties of an Essential Growth Factor for Pathogenic Bacteria

BY FELIX SAUNDERS, I. I. FINKLE, LEON STERNFELD AND STEWART A. KOSER

Many bacteria which develop quite readily in a meat-infusion culture-medium are unable to grow in a simple synthetic medium composed of several amino acids, dextrose, and inorganic salts. This observation is particularly true of many of the pathogenic types and has given rise to considerable speculation concerning the nature of the substances in meat infusions which appear to be necessary for development. Several attempts have been made to fractionate meat infusions or other similar mediums in the hope of gaining an insight into the nature of the factors essential for growth of the more exacting bacteria.[1] The same method of study has also been applied to yeasts.[2]

In previous work of our own[3] it was found that a growth-stimulating fraction could be removed from veal infusion by adsorption on charcoal and subsequent elution with hot ethanol or acetone. When this fraction was added to a simple synthetic medium[4] it rendered the medium suitable for the growth of some, though not all, of the more exacting pathogenic bacteria. In certain instances very small amounts of this added factor were sufficient to permit development in a synthetic medium in which the organisms ordinarily refused to grow. The results of a representative experiment with three microörganisms belonging to different biological groups are given in Table I.

The luxuriance of growth, varying from very light to heavy turbidity, is shown by the number of + signs. Absence of visible turbidity is shown by 0. An occasional doubtful reading is recorded ?. Readings were also made after seven and fourteen days, but have been omitted from the table as in most instances they showed no change.

The strain of *C. diphtheriae* used was a culture of "Park 8," that of the Sonne dysentery bacillus was no. 268 of the British Type Collection, and the strain of *Staph. albus* was from our laboratory stock collection.

Here it is seen that two of the three microorganisms refused to develop in the synthetic medium alone. The third organism, the so-called Sonne type of dysentery bacillus, grew very sparsely in the synthetic medium. When the fraction from veal infusion was added all of the organisms developed very well and produced a heavy growth in a few days. Relatively small amounts of this added material were effective and it is evident that something quite essential for multiplication has been added.

Is the added material a foodstuff or something in the nature of an accessory growth factor? It is obvious that the fraction from veal infusion must consist of a mixture of compounds and one would expect some food materials to be carried over along with any accessory factor which might be present. The results with the inorganic salt solution shown in Table I indicate that only a negligible amount of actual food material was contained

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(1) (a) Thjötta and Avery, *J. Exptl. Med.*, **34**, 97, 455 (1921); (b) Mueller, *J. Bact.*, **7**, 309 (1922); (c) Mueller, *et al.*, *ibid.*, **25**, 509 (1933); **30**, 513 (1935); (d) Whitehead, *Biochem. J.*, **17**, 742 (1923); **18**, 829 (1924); (e) Knight and Fildes, *Brit. J. Exptl. Path.*, **14**, 112 (1933); (f) Sahyun *et al.*, *J. Infectious Diseases*, **58**, 28 (1936).

(2) See especially Williams, *et al.*, THIS JOURNAL, **55**, 2912 (1933); *Proc. Soc. Exptl. Biol. Med.*, **32**, 473 (1934); Miller, Eastcott and Maconachie, THIS JOURNAL, **55**, 1502 (1933); Kögl, *Ber.*, **68, 16** (1928).

(3) Koser and Saunders, *J. Infectious Diseases*, **56**, 305 (1935).

(4) The synthetic medium consisted of 1.4 g. Na_2HPO_4, 1.0 g. KH_2PO_4, 2.0 g. NaCl, 0.1 g. $MgSO_4$, 3.0 g. asparagine, 0.1 g. cystine, 0.2 g. tryptophane, and 2.0 g. dextrose in 1 liter of distilled water. When an inorganic salt solution was desired for control purposes the asparagine, cystine, tryptophane and dextrose were omitted.

TABLE I

EFFECT OF ADDING A FRACTION FROM VEAL INFUSION TO A SYNTHETIC MEDIUM

Microörganisms used	Amount of added fraction,[a] cc.	Development in synthetic medium, days 1	2	4	Development in inorganic salt solution, days 1	2	4
Corynebacterium diphtheriae	None	0	0	0	0	0	0
	0.1	+	++	+++	0	0	0
	.01	0	+	++	0	0	0
	.001	0	0	+			
	.0001	0	0	0			
Shigella dysenteriae Sonne type	None	0	?	+	0	0	0
	0.1	+++	+++	+++	+	+	+
	.01	+++	+++	+++	0	?	?
	.001	+++	+++	+++	0	0	0
	.0001	+++	+++	+++	0	0	0
	.00001	+	+	+	0	0	0
Staphylococcus albus	None	0	0	0	0	0	0
	0.1	+	++	+++	?	+	++
	.01	0	+	++	0	0	0
	.001	0	0	0	0	0	0
	.0001	0	0	0	0	0	0

[a] The amount of solution of growth factor (from veal infusion) added to each 5-cc. tube of either synthetic medium or inorganic salt solution. The total solids in each cc. of the preparation of growth factor was 3 mg.

in the fraction from veal infusion. Since the inorganic salt solution supplied no food material which could be used by the bacteria for growth, any development following addition of the fraction from veal infusion must have resulted from food material carried over in this fraction. When large amounts such as 0.1 cc. of this preparation were added to the inorganic salt mixture, a light growth of two of the cultures resulted but in no case was the development nearly as rapid or as luxuriant as when a similar amount was added to the synthetic medium. Nor was growth stimulated by such small amounts of the fraction as was evident in the case of the synthetic medium. The preparation alone evidently supplied only traces of food material but when added to a synthetic medium containing dextrose and a few amino acids, very small amounts were sufficient to serve as an "activator" and the amino acids and dextrose were then utilized with resultant good development of the cultures.

Later work[5] showed that a similar preparation could be obtained from a considerable number of animal and plant sources. Of over thirty such sources tested, calf spleen, calf liver, and yeast appeared to be the richest. The evidence accumulated so far indicates that the growth factor is widely distributed in living tissue whether of plant or animal origin, and is probably a single chemical entity. Additional study of this apparently essential growth factor seemed desirable and attempts were made to obtain the active substance in pure form. Although this objective has not been reached up to the present time, some progress has been made in the fractionation, and with the partially purified preparations obtained it has been possible to study some of the chemical properties of the active principle.

Experimental

Preparation of Crude Growth Factor.—For the preparation of the fractions used in the following studies usually beef spleen or liver were used.[6] The method for concentrating growth factor has undergone several modifications. The process given below is the one in use at present. One hundred pounds (45 kg.) of beef spleen or liver are ground and covered with 250 liters of distilled water. After standing overnight or longer in the refrigerator the mixture is heated to boiling and boiled for five minutes. It is filtered while hot and the residue is washed with 50 liters of boiling water. The *hot* filtrates are combined and a *hot* saturated solution of lead acetate is added until no more precipitate is formed. It is important that *both* solutions be hot, otherwise the next filtration is likely to be very slow. Fuller's earth and supercel (200 g. of each) are stirred in thoroughly. The lead precipitate and the earths are filtered off. Charcoal is suspended in the filtrate (about 1 g. for every liter of filtrate added in small portions) and stirred intermittently for ten minutes or more. The charcoal is filtered off under suction and washed until free from lead.

The wet charcoal is placed in a large continuous extractor and extracted with alcohol for two weeks or more if the

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[5] Koser, Saunders, Finkle and Spoelstra, *J. Infectious Diseases*, **58** 12 (1936).

[6] We are indebted to Dr. David Klein of The Wilson Laboratories for generously supplying us with tissue and carrying out some of the preliminary steps of the purification.

alcohol still shows considerable color. The alcohol is changed every other day and the several portions of alcohol are combined. Every day 100 cc. of water is poured into the extractor through the condenser. When most of the color has been removed from the charcoal the extraction is discontinued and the charcoal discarded. The alcohol is removed from the combined extracts under reduced pressure. The residue is taken up in a minimum of water and any insoluble material is filtered off. The filtrate is again taken to dryness in a flask with a ground glass joint which can be fitted to a condenser.

The residue is extracted at least three times with 200-cc. portions of boiling absolute methanol. The methanol extracts are decanted or filtered from the residue in the flask. To the combined methanol extracts, 5 volumes of absolute ether are added. After standing a few minutes a gummy precipitate settles out leaving a clear supernatant fluid which can be decanted. The methanol–ether mixture is removed under reduced pressure. The residue is taken up in 100 cc. of water or more if necessary and any insoluble material is filtered off.

Fifty cc. of a 10% solution of chloroplatinic acid is added to the filtrate which is placed in the refrigerator and allowed to stand for a week or more. The precipitate which has formed is filtered off. The filtrate is allowed to stand overnight. If no more precipitate forms hydrogen sulfide is passed into the solution to remove the platinum. If a precipitate does form the filtrate is allowed to stand for a few days more and the second precipitate is removed.

After the platinum sulfide has been filtered off the filtrate is evaporated to dryness under reduced pressure. The residue is taken up in water and any insoluble material filtered off. The filtrate constitutes the crude material on which most of the tests described in this paper were performed. The solutions are straw colored or brownish and have a characteristic meat-extract odor. This odor is the same regardless of the source from which the material was prepared.

Method of Assay.—Four different organisms, *Staphylococcus albus*, *Corynebacterium diphtheriae* (Park 8), *Shigella dysenteriae* (Shiga), and *Brucella abortus*, were used for assay. These organisms show a wide range of sensitivity toward the growth factor but could always be arranged in the same order of sensitivity regardless of the source of the growth factor or the treatment to which it had been subjected. Throughout the experiments care was taken to avoid carrying over a heavy inoculum when testing for the presence of growth-promoting factor. Light suspensions of each of the four organisms were first made in 5 cc. of a buffered salt solution by transferring a small bit of growth from a twenty-four- or forty-eight-hour agar slant of the culture. These suspensions showed no evident turbidity. After thorough distribution, 0.1 cc. of the suspension was then pipetted aseptically into each tube of synthetic medium containing the added extract and also into controls of synthetic medium alone and of veal infusion broth. All tests were incubated at 37°. Throughout the work the purity of the cultures developing in the various tests was often checked by gram stains together with whatever other study appeared desirable.

Solubility in Organic Solvents.—A solution of growth factor was shaken with three separate portions of ether. The ether fractions were combined and the ether removed under diminished pressure. The slight residue was taken up in water and assayed but no activity could be detected. Similar results were obtained from the same procedures using benzene and chloroform. The higher alcohols appear to dissolve some growth factor but the growth factor is probably held in the small amount of water which the alcohols dissolve. The growth factor is soluble in absolute methanol and absolute ethanol but not as readily as in water. However, it is still too soluble in these alcohols to permit recrystallization from them. In one experiment a concentrated solution of growth factor in ethanol was prepared and chilled with solid carbon dioxide until it became sirupy but no solid was thrown out. Of course the growth factor is readily soluble in any aqueous mixture of the alcohols since it is extremely soluble in water.

Solubility in Phenol.—A growth-factor preparation was evaporated to dryness. Phenol was added and warmed until it liquefied. All of the material appeared to go into solution. The flask was washed out with another portion of liquefied phenol and the combined portions of phenol were filtered through a steam funnel. The phenol was removed from the filtrate by steam distillation. The liquid remaining in the flask after removing the phenol was evaporated to dryness under diminished pressure, taken up in the original amount of water and assayed. Little or none of the activity had been destroyed by the treatment described.

Effect of Oxidants on Growth-Factor Preparations.—Enough 30% hydrogen peroxide was added to 50 cc. of a solution of growth factor to give a final concentration of 3% and the solution heated on the steam-bath for forty-five minutes. The solution was evaporated to dryness under reduced pressure and the residue taken up in 50 cc. of water. Another sample of growth factor in aqueous solution was aerated by passing a vigorous stream of air through a flask containing the solution for twenty hours. Enough water was then added to restore the original volume. Assay showed that in neither of these samples was the activity appreciably diminished. Heating a sample of growth factor on the steam-bath under reflux for thirty-six hours or autoclaving for fifteen minutes at 1 atm. extra pressure had no detectable effect on the activity.

Action of Bromine on Growth Factor.—Bromine was added drop by drop to a solution of growth factor with vigorous shaking until the color persisted. The solution was allowed to stand overnight in a refrigerator. Excess bromine was removed by aeration and a gummy precipitate which had formed was filtered off. Silver acetate was added to remove bromide ions and the silver bromide removed by filtration. Hydrogen sulfide was passed into the solution and the silver sulfide formed was filtered off. The filtrate was concentrated under reduced pressure to dryness and then taken up in enough water to make up the original volume of the solution. The activity had been reduced by about one-fourth. In another experiment the bromine was added in solution in chloroform. The results were essentially the same as described above. When a large excess of liquid bromine is added to a dried growth-factor preparation and heated on the steam-bath the activity is destroyed completely.

Action of Ammoniacal Silver on Growth Factor.—Ammoniacal silver was added to a growth-factor preparation and the solution was warmed on the steam-bath for ten minutes. The calculated amount of hydrochloric acid was added and the silver chloride removed. There was no loss of activity. None of the preparations tested reduced Fehling's solution.

Action of Acetic Anhydride on Growth Factor.—A solution of growth factor was evaporated to complete dryness *in vacuo*. Seventy-five grams of acetic anhydride and 5 g. of fused sodium acetate were added. The mixture was heated on the steam-bath under reflux for twenty minutes and then poured into 500 cc. of iced water. A gummy precipitate formed which was removed by filtration. The filtrate was diluted to 2 liters and treated with 15 g. of charcoal in two steps to adsorb the growth factor. The charcoal was filtered off and extracted in a continuous extractor for twenty-four hours. The alcohol was removed under reduced pressure and the residue taken up in water. Assay showed that there had been only a slight loss of activity.

Action of Nitrous Acid on Growth Factor.—Fifty cc. of a preparation was diluted to 2 liters and 10 g. of sodium nitrite added. The solution was cooled to 10° and 25 cc. of glacial acetic acid added. The solution was stirred for thirty minutes and then allowed to stand overnight in the refrigerator. The growth factor was adsorbed on 8 g. of charcoal and eluted with alcohol. There was only a slight loss of activity.

Qualitative Elementary Tests.—Qualitative tests for nitrogen were run on several different samples. In every case the test was positive. Tests for sulfur run on the same samples were always negative. Since the preparations were impure no significance can be attached to the nitrogen tests but the growth factor is probably free from sulfur.

Discussion

All the experiments described above have been repeated and confirmed several times. They have also been repeated in many cases using growth factor from different sources. All the evidence at hand indicates that the growth factor is the same regardless of source and that it is a widely distributed if not universal constituent of living tissue. Many microörganisms are unable to utilize sources of energy unless this accessory substance is present. Others which are capable of developing in a synthetic medium apparently can either get along without it or can synthesize the small amount of growth factor that they need. For example, veal infusion from which the growth factor has been removed by adsorption on charcoal will still support the growth of airborne saprophytes and molds but will not permit the growth of certain pathogens. However, after saprophytes have been allowed to grow in the infusion which has been treated with charcoal the presence of growth factor can be demonstrated by the technique described above. Furthermore molds grown on Czapek-Dox medium will synthesize growth factor.

Because of the wide distribution of growth factor and the organisms capable of synthesizing it, it would be difficult or impossible to produce a diet deficient in this factor for higher forms, especially as the intestinal tract contains organisms capable of synthesizing this accessory. Growth factor requirements can be studied only under rigidly controlled conditions such as those prevailing in bacterial cultures in a synthetic medium. Perhaps organisms in the intestinal tract play an essential part in supplying this factor and are a part of a true symbiosis.

There is considerable variation among bacteria regarding their growth-factor requirements. Some require only a few micrograms of growth factor for each liter of medium in order to produce abundant growth while others grow much less vigorously even when the amount of growth factor has been increased as much as a hundred fold. Of course, many other factors such as amino acids, sugars, etc., may be involved. Cultures of *C. diphtheriae* have been grown on synthetic medium plus growth factor by transferring directly from one synthetic culture to another without any intermediate culturing on infusion. This culturing has been carried on for over fifty successive transfers.

In spite of its biological reactivity, growth factor is comparatively unreactive chemically. Although it has the stability generally associated with hydrocarbons it is extremely water soluble. Dried growth-factor preparation dissolves in water almost instantaneously but is not hygroscopic. It probably is not inorganic since it is destroyed by both wet and dry ashing. At present we feel that we have not enough positive chemical evidence at hand to warrant drawing any conclusions regarding its chemical constitution.

Acknowledgment.—This work has been aided by a grant from the Committee on Scientific Research of the American Medical Association. It is a pleasure to be able to thank the Committee for their generous support.

Summary

1. Many plant and animal tissues contain a substance which is essential for the growth of certain pathogenic bacteria. This substance has been purified partially and the chemical properties of the impure preparations studied.

2. Growth factor is soluble in water, metha-

nol, ethanol, and phenol, but it is insoluble in the higher alcohols, ether, benzene, and chloroform.

3. The activity is not appreciably affected by autoclaving, aeration, boiling, or by oxidizing agents such as 3% hydrogen peroxide, or ammoniacal silver, and is only slightly affected by bromine in the cold.

4. Treatment with acetic anhydride caused only slight loss of activity.

5. The growth factor probably does not contain sulfur.

6. It is not inorganic since it is destroyed by both wet and dry ashing.

CHICAGO, ILL. RECEIVED NOVEMBER 14, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CHICAGO]

Studies in Proteins. V. A Crystalline Globulin from the Paradise Nut, Lecythis Zabucayo

BY BIRGIT VENNESLAND, MARY B. BLAUCH AND FELIX SAUNDERS

Introduction

The Paradise nut, *Lecythis zabucayo*, is a rugose, fusiform nut resembling the Brazil nut in size and taste. It is grown in Brazil and Guiana where it is known as the sapucaya or monkey-pot nut. The natives consider the flavor of the Paradise nut to be superior to that of the Brazil nut, consequently few of them are exported but they can be obtained occasionally on the Chicago market.

Since the Brazil nut yields a crystalline globulin, excelsin, it was thought possible that the Paradise nut might also yield a crystalline globulin.

Method.—A protein was isolated from Paradise nuts by extracting the defatted seed-meal with a saturated solution of sodium chloride and precipitating the protein with ammonium sulfate. The precipitate formed by saturating the protein solution with ammonium sulfate was redissolved in water and dialyzed against running distilled water at about 5°. Details of the method have been given elsewhere.[1] During dialysis crystals of globulin formed in the viscose bags. The crystals were thick, hexagonal plates. The edges of the upper and lower surfaces appeared to be beveled. Three of the angles of the sides were slightly more acute than those of the other three.

Experimental

Determinations of nitrogen distribution were made in the usual way. The results given below represent an average of several determinations.

	Protein, % Paradise-nut globulin	Protein, % Excelsin[a]	Total N, % Paradise-nut globulin
Amide N	1.42	1.48	9.12
Humin N	0.33	0.17	2.10
Total N in phosphotungstic acid ppt.	5.54	5.76	35.60
α-Amino N in phosphotungstic acid ppt.	2.06		13.28
Total N in filtrate (Kjeldahl)	8.46	10.97	53.51
α-Amino N in filtrate (Van Slyke)	8.43		53.44
Total N	15.75	18.30	
Histidine N (colorimetric)			5.23
Cystine N (gravimetric)			0.47

[a] Osborne and Harris as quoted by Plimmer, "Chemical Constitution of the Proteins," 2nd ed., Longmans, Green and Co., New York, 1924, p. 131.

Summary

A crystalline globulin has been isolated from the Paradise nut (*Lecythis zabucayo*).

The nitrogen distribution of this protein has been determined and found to be the same as excelsin except for mono-amino nitrogen.

CHICAGO, ILL. RECEIVED NOVEMBER 27 1936

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(1) Saunders, THIS JOURNAL, **53**, 696 (1931).

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

Nitrogen Compounds in Petroleum Distillates. IX. Nitrogen Bases from California Cracked Gasoline[1]

BY A. C. BRATTON AND J. R. BAILEY

The crude bases for this investigation, 242 cc., b. p. 115-240°,[2] were extracted from four barrels of pressure distillate, b. p. 36–171°, obtained in cracking *gas-oil*, from Los Angeles Basin petroleum, and *crude residuum* from San Joaquin Valley petroleum, at 454° and 54–58 atmospheres.

Nine bases, consisting of quinoline, quinaldine, and seven pyridine homologs, were isolated and there is no reason to suspect that any base, present beyond negligible amount, was overlooked. *Non-aromatic* types, which are present along with *aromatic* types in *straight-run* kero bases in a percentage ratio of approximately 85:15, respectively,[3] were not encountered among the *cracked* gasoline bases which obviously are pyrolysis products of more complex molecules, including aromatic and non-aromatic bases together with inert nitrogen compounds.[4] At the temperature of the cracking plant non-aromatic bases are evidently unstable and, it may be, undergo dehydrogenation and molecular rearrangement to more stable aromatic types. Whereas both quinoline and quinaldine occur in cracked gasoline, a careful search carried out in the Texas Laboratory has not revealed either of these products or any monoalkyl quinoline in straight-run distillates. Since a number of polymethylated quinolines have been identified in straight-run distillates, dealkylation may be assumed as at least one effect produced at high temperatures on aromatic bases and it is equally certain that, through pyrolytic degradation of polynuclear aromatics, there arise at times pyridine or its homologs.

Due to the limited supply (130 cc.) of bases available, it was impractical to fractionate this small volume exhaustively through an effective column by the usual procedure. To circumvent this difficulty, resort was had to the indirect micro method, termed Amplified Distillation,[5] which originated with the authors.

An inspection of Table I reveals that, because of the proximity of boiling points (144–145.3°, 157–158°, 170.3–171.6°) within three pairs of the gasoline bases, it was impractical to separate individual products, free of admixtures, through fractional distillation alone.

Experimental

Action of *p*-Toluenesulfonyl Chloride on the Bases.—The crude material (154.5 cc. or 139.3 g.) was added to 851 cc. of 3 *N* sodium hydroxide and 272 g. of *p*-toluenesulfonyl chloride was stirred in over a period of forty-five minutes with the temperature at 25–30°. A temperature of 60–70° was then maintained for fifteen minutes, after which the cooled solution (A) was extracted with several 200-cc. portions of ether (B), followed by withdrawal of the bases (112 cc.) from the latter with four 200-cc. portions of 1 *N* hydrochloric acid. Since there was no precipitation of sulfonamides on strong acidification of the ethered out solution (A), it was evaporated to dryness, 400 cc. of concentrated hydrochloric acid was added and the mixture was refluxed for thirty hours. After removal of the excess acid in steam, caustic soda was added and the free bases (18 cc.) were distilled out with steam. These bases proved to be exclusively tertiary and accordingly were combined with the 112 cc. of unchanged bases recovered from the toluenesulfonyl chloride treatment. The residue from evaporation of the ether solution (B) on being processed like solution (A) yielded no bases. From these results it is evident that the Hinsberg separation of amines is unreliable when applied to a complex mixture of petroleum bases.

Amplified Distillation.—To the 130 cc. of bases was added 2438 cc. of acid- and caustic-washed hydrocarbon oil boiling evenly over a 90–240° range. This mixture was distilled at a 10:1 reflux ratio through a 1 × 105-cm. spirally-indented, adiabatic column, cuts being made in 1° fractions (D). A second fractionation from a smaller still-pot was performed as follows: the still was charged with the lowest fraction, 1D, which was then topped in 1° cuts to the minimum temperature of 2D, when this second fraction was added. The procedure was repeated in ascending order of boiling points until all the D fractions were distilled. Finally a third distillation was carried out in like manner on the fractions from the second distillation. The final 1° cuts from multiple distillation boiled over a 35–260° range, with the bases segregated between 98–236°, *i. e.*, in 139 fractions, each with an average base content of around 1 cc.

The base-hydrocarbon fractions were agitated over three-minute periods with three successive 0.5–0.7 volumes of 4 *N* hydrochloric acid, followed by 0.5 volume of water. In order to withdraw *non-aromatic hydrochlorides* each of the acid extracts was agitated for thirty minutes with an equal volume of chloroform.[3] A very small amount of

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[1] From a dissertation presented by A. C. Bratton to the Faculty of the Graduate School of the University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] This material was assembled by the Union Oil Company of California.

[3] T. S. Perrin and J. R. Bailey, THIS JOURNAL, **55**, 4136 (1933).

[4] *Cf.* E. J. Poth, *et al.*, *ibid.*, **52**, 1240 (1930).

[5] Bratton, Felsing and Bailey, *Ind. Eng. Chem.*, **28**, 424 (1936).

TABLE I

BASES FROM PRESSURE DISTILLATE

Product	B. p.,[9] °C.	n^{25}_{D}[9]	Isolated as	M. p. crude salt, °C.	Salt no.	Wt. of salt, mg.	Source of fractions	M. p. pure salt, °C.		
								Eguchi[7]	Beilstein[8]	This work
2-MP[a]	129.3	1.4983	Picrate	164–165	1	782	98–118	165	164, 165	165.5
2,6-DMP	144	1.4953	Picrate	162–163	2	181	128–135	162	161	163
4-MP	145.3	1.5029	Picrate	162–165	3	617	119–129	167	167	167
2,5-DMP	157	1.4982	$HgCl_2$ salt	201–203	4	621	142–150	197[9]	162–164	168.5–169.5
			picrate					167	151–152 156–157 165.5	
2,4-DMP	158	1.4984	Picrate	181–183	5	139	137–140	182	179	182.5–183
			$HgCl_2$ salt	130–131	6	2688	142–156	131–132	132	131.5–132
			picrate	172–173.5	7	50	Bases from picrates E[b] 158–173			
2,4,6-TMP	170.3	1.4959	$HgCl_2$ salt	154–155	11	2784	155–167		154	
			picrate	154–155	12	420	Bases from picrates E 163–173	157	155–156 155–156	155.5–156
3,5-DMP	171.6	1.5032	$HgCl_2$ salt	253–259	8	496	142–167			
			$HgCl_2$ salt	168–169	9	384	155–162		170	
			picrate	242.5–243.5	10	20	Bases from picrates E 168–173	244	172–173 228–230	245
Quinoline	238.1[10]	1.6245[8]	Picrate	202–204	13	1270	199–220		203	203–203.5
2-MQ	247.6[10]	1.6093[8]	Picrate	190–193	14	125	225–233		191	193–194

[a] MP = Methylpyridine; DMP = Dimethylpyridine; TMP = Trimethylpyridine; MQ = Methylquinoline.
[b] See below, "Treatment of Unresolved Bases."

bases recovered from the combined chloroform extracts proved to be *aromatic*. From this result, *the occurrence of non-aromatic bases in cracked gasoline, regardless of its source, is not to be expected;* in any event, so far as concerns the processing of the bases under investigation, chloroform extraction of their hydrochlorides was superfluous.

In order to remove chloroform, the separate acid fractions were steamed out and the bases were freed with caustic and distilled in steam. Sulfur dioxide was then run into the separate distillates to methyl orange acidity, excess picric acid solution was added and precipitation was allowed to proceed under thermostatic control over four-hour periods at 50, 35° and finally at the minimum temperature allowable without separation of picric acid.

Water saturated with sulfur dioxide will not precipitate picric acid from its aqueous solution saturated at the same temperature; so temperature–solubility curves of picric acid in water[6] made possible a regulation of the minimum temperature at which picration could be effected with avoidance of any separation of picric acid.

Where picrates were not freed of admixtures through recrystallization, they were converted to mercuric chloride salts and an exchange in the two types of salts was repeated as often as necessary for final purification. The confusion which often arises from the formation of different mercuric chloride salts of an individual base was eliminated by observance of specific conditions which led to definite products, usually of the formula $Base{\cdot}HCl{\cdot}2HgCl_2$. For conversion of a picrate to a mercuric chloride salt, the base was liberated, steam distilled and titrated to slight acidity (methyl orange) with 0.506 *N* hydrochloric acid. Through the use of a mercuric chloride solution saturated at 25°[6] (p. 409) it was possible to carry out precipitation with exactly 2 moles of mercuric chloride per mole of base-hydrochloride. Minimum allowable cooling curves were again used as controls in fractional precipitation of the salts over a maximum temperature range. Where a salt appeared with a mercury content greater than in the formula $Base{\cdot}HCl{\cdot}2HgCl_2$, an adjustment was made in the amount of the reagent, such as to ensure complete precipitation of the bases.

Table I summarizes the properties of the salts obtained from the amplified distillation fractions. In recombination of individual salts from various fractions, prior to their purification and identification, it is obvious from the wide overlap of the origin of the corresponding bases, that the salts were combined from broader bands of distillation fractions than might seem warranted.

Treatment of Unresolved Bases.—In order to rework the regained residual bases from the salts described above, they were dissolved in 1 liter of sulfurous acid solution, excess picric acid (15 liters) was added and the bases were liberated from both the precipitated (D) and dissolved (E) picrates. This material gave the following constants.

	Cc.	G.	B. p., °C.	n^{25}_{D}	Sp. gr. 28.5/25.6
Bases from D	29	26.6	116–225	1.5002	0.9172
Bases from E	27.5	25.1	116–200	1.4953	.9157

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(6) Seidell, "Solubilities of Inorganic and Organic Compounds," 2d ed., D. Van Nostrand Co., New York, 1919, p. 492.

(7) Eguchi, *Bull. Chem. Soc. Japan*, **2**, 176 (1927); **3**, 227, 235 (1928); *Chem. Zentr.*, **98**, 1223 (1927); **100**, 331 (1929).

(8) Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. XX, 1935.

(9) Errera, *Ber.*, **34**, 3700 (1901).

(10) Michael, *Ber.*, **18**, 2020 (1885).

The bases from E, *without admixture with hydrocarbon oil*, were fractionated in the usual way into 5° cuts through a 1 × 105-cm. column with a 10:1 reflux ratio. Crystalline salts were obtained from all of the first seven fractions boiling up to 164°; the remainder yielded only smears. Final purification through an exchange in salt types was effected as follows: mercuric chloride salts ⟶ picrates ⟶ mercuric chloride salts ⟶ picrates. The products isolated and identified as picrates were 2,4-dimethylpyridine, 3,5-dimethylpyridine and 2,4,6-trimethylpyridine; in other words, the presence of only three of the nine bases (Table I) identified through amplified distillation could be confirmed. This comparison establishes beyond question the superiority of amplified distillation over straight distillation in the resolution of complex mixtures of petroleum bases.

The bases from (D) were processed similarly to those from (E) but no pure individual product was isolated.

Purification and Identification of Salts

Each of the salts listed below was synthesized for a comparison of the two samples by solubilities, crystalline form and mixed melting points.

2-Methylpyridine.—Picrate 1 was recrystallized from water in long (2 cm.) spear-like clusters of slender prisms melting at 165.5°.

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: N, 17.39. Found: N, 17.51.

4-Methylpyridine.—Picrate 3 was recrystallized from water in clusters of flat feather-like needles (1.5 cm.) melting at 167°.

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: N, 17.39. Found: N, 17.55.

2,6-Dimethylpyridine.—Picrate 2 was recrystallized from water in microscopic prisms melting at 163°.

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.45.

2,5-Dimethylpyridine.—The mercuric chloride salt 4 was converted to the picrate which crystallized from water in long (2 cm.) spear-shaped clusters of thin prisms melting at 168.5–169.5°. The synthetic picrate prepared by the method of Errera[9] (p. 3691) melted at 167.5–168.5° (Errera reported 165.5°).

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.43.

2,4-Dimethylpyridine.—Picrate 5 from water formed slender prisms melting at 182.5–183° in agreement with the synthetic product, m. p. 182.5°.[10] The picrate is far less easily purified than is the mercuric chloride salt.

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.49.

3,5-Dimethylpyridine.—Picrate 10 separated from water in single slender needles (5 mm.) melting at 245°.

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.91.

2,4,6-Trimethylpyridine.—Picrate 12 crystallized from water in short interlacing needles melting at 155.5–156°.

Anal. Calcd. for $C_{14}H_{14}O_7N_4$: N, 16.00. Found: N, 16.12.

Quinoline.—Picrate 13 crystallized from 50% alcohol in very short needles melting at 203–203.5°.

Anal. Calcd. for $C_{15}H_{10}O_7N_4$: N, 15.64. Found: N, 15.65.

Quinaldine.—The melting point of picrate 14 after several recrystallizations from acetone rose from 191–192° (reported in the literature) to 193–194°. This solvent is to be preferred to water or alcohol. Nitrogen determination on the lower melting sample ran 0.3–0.5% below the calculated per cent.

Anal. Calcd. for $C_{16}H_{12}O_7N_4$: N, 15.05. Found: N, 14.98.

Summary

Seven pyridine homologs, quinoline and quinaldine were isolated through *amplified distillation* of 130 cc. of California pressure distillate gasoline bases. In contrast to *straight run* distillates in the same temperature range, which contain in preponderant amount *non-aromatic* bases, only *aromatic* bases were encountered in the *cracked* gasoline.

The present investigation offers conclusive proof of the efficiency of amplified distillation as an indirect micro method in exhaustively fractionating small volumes of complex mixtures of petroleum bases.

AUSTIN, TEXAS RECEIVED NOVEMBER 16, 1936

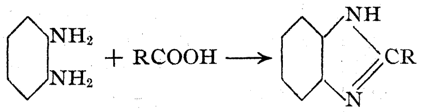
[Contribution from the Research Laboratory of Armour and Company]

2-Alkylbenzimidazoles as Derivatives for the Identification of Aliphatic Acids

By W. O. Pool, H. J. Harwood and A. W. Ralston

In the course of work involving the identification of normal fatty acids the need of a complete series of satisfactory derivatives became apparent. Of the various derivatives described in the literature for the characterization of organic acids the 2-alkylbenzimidazoles of Seka and Müller[1] appeared most promising.

These 2-alkylbenzimidazoles were prepared by heating a mixture of the acid and *o*-phenylenediamine. The resulting compounds were comparatively high melting and the melting point range of the series was continuous and broad.



The series of 2-*n*-alkylbenzimidazoles through the *n*-heptadecyl derivative has now been completed. The procedure of Seka and Müller has been improved in that the time required for the preparation of a derivative has been greatly reduced and the compounds obtained by the present method have been found to possess higher melting points than those reported by Seka and Müller.

Experimental Part

Procedure.—A mixture of 1 to 3 g. of acid and a molecular equivalent of *o*-phenylenediamine was heated at the boiling temperature for thirty minutes. The mixture was then dissolved in hot alcohol and the unreacted acid neutralized by the addition of potassium hydroxide solution until just alkaline to phenolphthalein. In the case of capric and higher acids the 2-alkylbenzimidazole crystallized when this alcohol solution was cooled. In the case of pelargonic and lower acids ether was added to the alcohol solution and this ether solution then washed with successive portions of water. The 2-alkylbenzimidazole was obtained by evaporation of the ether. The products were purified by recrystallization from alcohol, dilute alcohol or water with the addition of decolorizing carbon.

Table I

Constants for 2-*n*-Alkylbenzimidazoles

n-Alkyl	M. p. (corr.),[i] °C.	Mixed m. p. with[j] next higher homolog (corr.), °C.	Analyses,[k] % N Calcd.	Found
Hydrogen[a,n]	172.0–173.0	130–132	23.73	23.81
Methyl-[b,m,n]	177.0–177.5	157–158	21.21	21.42
Ethyl-[c,m,n]	174.5	155–156	19.18	19.03[o]
n-Propyl-[d,l,m]	157.0–157.5	141–143	17.50	17.76
n-Butyl-[e,m]	155.0–155.5	152–153		
n-Pentyl-[c,l,m]	163.0–163.5	138–143	14.89	14.88[p]
n-Hexyl-[c,m]	137.5–138.0	132–135	13.86	14.04
n-Heptyl-[c,l]	144.5–145.0	136–137	12.96	12.97
n-Octyl-[c]	139.5–140.5	128–131	12.17	12.11[q]
n-Nonyl-[c,l]	127.0–127.5	117–120	11.47	11.80
n-Decyl-[c]	114.0–114.5	106–107	10.85	11.06
n-Undecyl[f,l]	107.5	107–108	10.29	10.27[r]
n-Dodecyl-[c]	109.0–109.5	105–106	9.79	10.05
n-Tridecyl-[c]	105.0–105.5	100–102	9.33	9.47
n-Tetradecyl-[g]	98.5– 99.5	97– 98	8.91	9.46[s]
n-Pentadecyl-[c,l]	96.5– 97.0	94– 96	8.53	8.62
n-Hexadecyl-[c]	93.5– 94.5	93– 94	8.18	8.52
n-Heptadecyl-[h,l]	93.5– 94.5		7.86	8.08[t]

[a] The acid was Baker c. p. 90% grade. [b] The acid was Baker c. p. glacial acetic acid. [c] The acid was Eastman best grade. [d] The acid was obtained by fractionation of Merck technical grade (98–100%). [e] The acid was synthesized from *n*-butyl bromide by means of the Grignard reagent and carbon dioxide; b. p. 185.0–185.6°. [f] The acid was obtained from coconut oil by fractionation of esters and subsequent recrystallization of the acid from acetone; m. p. 44.0–45.0°. [g] The acid was synthesized from Eastman myristic acid by the usual method: acid ⟶ ester ⟶ alcohol ⟶ iodide ⟶ nitrile ⟶ acid. Recrystallized from acetone; m. p. 52.5–53.5°. [h] The acid was obtained by fractionation of hydrogenated ethyl oleate followed by recrystallization of the acid from acetone; m. p. 70.0–71.0°. [i] M. p. thermometer standardized against known substances. [j] M. p. of a 50% mixture with next higher homolog. [k] Analyses by Dr. Ing. A. Schoeller, Berlin–Schmargendorf, Tolzerstrasse 19, except the analysis of *n*-tetradecylbenzimidazole which was by Dr. Kurt Eder, University of Illinois, Urbana, Illinois. [l] Previously prepared by Seka and Müller.[1] [m] See Weidenhagen, *Ber.*, **69**, 2263 (1936). [n] See Phillips, *J. Chem. Soc.*, 2393 (1928). [o] Calcd.: C, 73.93; H, 6.90. Found: C, 74.06; H, 6.90. [p] Calcd.: C, 76.54; H, 8.57. Found: C, 76.71; H, 8.71. [q] Calcd.: C, 78.19; H, 9.63. Found: C, 78.43; H, 9.68. [r] Calcd.: C, 79.34; H, 10.37. Found: C, 79.54; H, 10.41. [s] Calcd.: C, 80.18; H, 10.90. Found: C, 80.13; H, 10.52. [t] Calcd.: C, 80.82; H, 11.31. Found: C, 80.67; H, 11.19.

Discussion

2-Alkylbenzimidazoles were easily and quickly prepared from small amounts of material. These derivatives crystallized well and possessed sharp melting points. With the lower members of the series the melting point interval between adjacent members was large and there was considerable depression in the melting point of mixtures of adjacent members. The 2-alkylbenzimidazoles of acids above lauric did not serve as a very good means of distinguishing these acids from one

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[1] Seka and Müller, *Monatsh.*, **57**, 95–105 (1931).

another as the melting points of these derivatives lay closely together. In certain cases the compounds contained a colored impurity which was removed only after numerous crystallizations.

These 2-alkylbenzimidazoles form salts with acids (picric, sulfuric, etc.) which might be used in distinguishing the higher members of the series. This possibility has not yet been investigated.

Summary

1. A procedure for the preparation of 2-alkylbenzimidazoles from aliphatic acids and *o*-phenylenediamine has been described.

2. A series of 2-alkylbenzimidazoles has been prepared using normal aliphatic acids containing from one to eighteen carbon atoms.

CHICAGO, ILL. RECEIVED OCTOBER 28, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

The Liquidus Curve and Surface of the Systems Lithium and Calcium Nitrates and Calcium, Lithium and Potassium Nitrates

BY ALEXANDER LEHRMAN, EDWARD ADLER, JACOB FREIDUS AND MAX NEIMAND

This paper reports an investigation of the liquidus curve and surface of the systems lithium and calcium nitrates and calcium, lithium and potassium nitrates. The work was undertaken in order to be able ultimately to define the liquidus surfaces of the quaternary system composed of the nitrates of lithium, sodium, potassium and calcium. It is hoped that the quaternary system in mind will yield a salt-bath melting below 100°. Such a salt-bath would have distinct advantages.

Of the six binary and four ternary systems that should be known before the quaternary system is investigated, five binary and two ternary are described in the literature.[1]

The completion of the present work leaves uninvestigated only the ternary system lithium, sodium and calcium nitrates (although it seems necessary in the light of the work of Rostkovsky,[1f] of Laybourn and Magdin[1g] and the data presented here, that the ternary system composed of the nitrates of sodium, potassium and calcium as presented by Menzies and Dutt[1b] should be checked).

Experimental

The salts used were prepared from C. P. products by recrystallization followed by drying except the calcium nitrate which was the C. P. salt dissolved, treated with pure lime, filtered, neutralized with nitric acid, evaporated and dried.

Temperature Measurements.—Temperatures were measured with a copper–constantan thermocouple of No. 28 wire in conjunction with a Leeds and Northrup potentiometer indicator, the cold junction being cracked ice. The couple was protected from the molten nitrates by a narrow guard tube made by drawing out Pyrex tubing and sealing at one end. It was standardized by determining the e. m. fs. at the boiling point of water and melting points of U. S. Bureau of Standards tin (231.9°), C. P. cadmium (320.9°), and purified potassium dichromate (397.5°), and plotting the deviations from the standard table of Adams.[2] While the melting point of potassium dichromate is about 10° higher than the upper end of the standard table, it was considered justifiable to extrapolate through this short range.

Method.—Mixtures of the two salts (approximately 20 g.) were made in the 2.5 × 20-cm. Pyrex tubes used in the determinations. The couple in its guard tube was inserted into the salt mixture and held in place by a two-holed stopper. A stirrer made of Pyrex rod passed through a piece of Pyrex tubing in the second hole of the stopper. It was necessary to use Pyrex glassware throughout, as molten lithium nitrate attacks soft glass.

The tube holding the salts was suspended in a small resistance furnace and heated while stirring until the salts were completely molten, care being taken to avoid excessive temperatures. It was then transferred to a double-walled test-tube and held suspended there by an asbestos ring, and constantly stirred.

As the crystallization temperature was approached, crystals formed on the test-tube wall at the surface of the molten salt and were pushed into the liquid by the stirrer. The initial crystallization temperature was seen easily, as clouds of fine crystals suddenly appeared, while above this temperature the crystals when pushed into the melt by the stirrer rapidly dissolved. No supercooling was observed in any of the stirred melts, except in the calcium nitrate region of the ternary system, where it was necessary in some cases to inoculate with very fine crystals in order to prevent the formation of supercooled glasses which when formed did not crystallize on long standing. Crystallization temperature determinations were repeated until they agreed to within 1.0°. The reported values represent at least three determinations.

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[1] (a) Carveth, *J. Phys. Chem.*, **2**, 209 (1898); (b) Menzies and Dutt, THIS JOURNAL, **33**, 1366 (1911); (c) Amadori, *Atti inst. Veneto*, **72**, 451 (1912); (d) Harkins and Clark, THIS JOURNAL, **37**, 1816 (1915); (e) Briscoe and Magdin, *J. Chem. Soc.*, **123**, 1608, 2914 (1923); (f) Rostkovsky, *J. Russ. Phys.-Chem. Soc.*, **42**, 2055 (1930); (g) Laybourn and Magdin, *J. Chem. Soc.*, 2582 (1932), 236 (1933); (h) Laybourn, Magdin and Freeman, *ibid.*, 139 (1934).

[2] "Pyrometric Practice," Bureau of Standards Technological Paper No. 170, p. 309.

The Binary System Lithium and Calcium Nitrates.—In order not to overlook any break in the liquidus curve, time–temperature and time–differential temperature cooling curves were made on a number of melts. No halt due to a transition or reaction was observed. These curves showed the eutectic temperature of the system to be at 235.2°. The apparatus used for the time–temperature and time–differential temperature cooling curves has been described previously.[3] It should be mentioned that when stirring is omitted as was the case in obtaining the cooling curves, supercooling takes place at the initial crystallization temperature and slight supercooling at the eutectic point.

Decomposition was not apparent in any of the melts until the concentration of calcium nitrate reached 60%. By slow and careful heating of this mixture decomposition was reduced to a negligible amount. The observed melting points are recorded in Table I and plotted in Fig. 1.

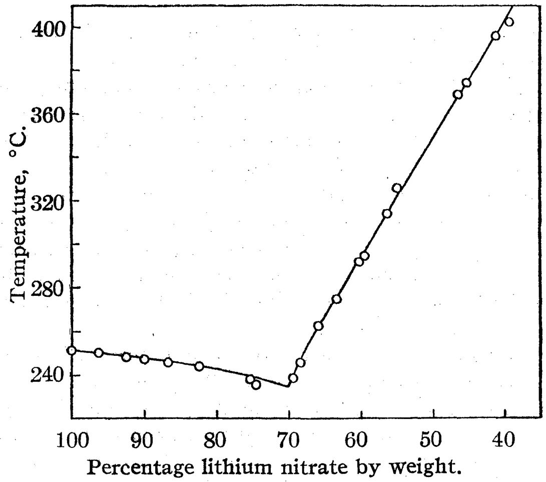

Fig. 1.—Liquidus of the lithium nitrate–calcium nitrate system.

The melting point of lithium nitrate found (251.4°) agrees well with that determined by Briscoe, Evans and Robinson (252°).[4]

TABLE I

CRYSTALLIZATION TEMPERATURES. LITHIUM NITRATE–CALCIUM NITRATE

$LiNO_3$ wt. %	Temp., °C.	$LiNO_3$ wt. %	Temp., °C.
100.0	251.4	66.0	263
96.2	250	63.5	274
92.4	248	60.3	292
90.0	247	59.5	294
86.7	246	56.3	314
82.2	244	55.0	326
75.3	237	46.5	369
74.6	235	45.3	374
69.4	238	41.2	396
68.4	246	39.4	403

The Ternary System Lithium, Potassium and Calcium Nitrates.—The region near the 100% calcium nitrate point was not investigated as calcium nitrate decomposes before it melts. In all cases care was taken not to heat the mixtures above 400° to avoid decomposition. Furthermore, no effort was made to find the boundaries of the region in which the compound $4KNO_3 \cdot Ca(NO_3)_2$ is formed from the melt. The determination of a few points in the binary system potassium and calcium nitrate showed that Rostkovsky's results[1f] are more reliable than those of Menzies and Dutt.[1b] In the region of high concentration of

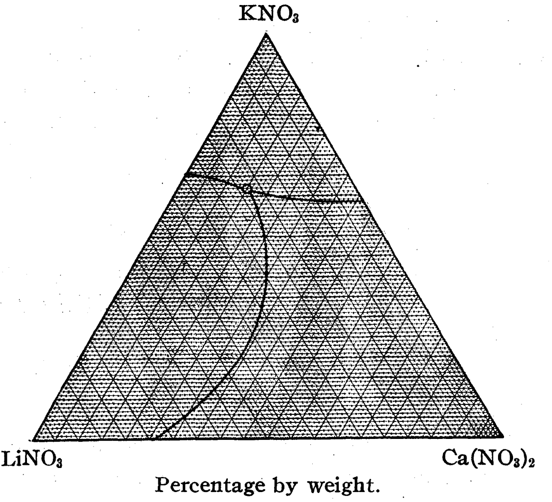

Fig. 2.—Liquidus surface of the system lithium, potassium and calcium nitrates.

TABLE II

CRYSTALLIZATION TEMPERATURES: LITHIUM, POTASSIUM AND CALCIUM NITRATES

$LiNO_3$ wt. %	KNO_3 wt. %	Temp., °C.	$LiNO_3$ wt. %	KNO_3 wt. %	Temp., °C.
36.3	29.5	211	70.0	9.9	236
27.8	23.9	304	50.1	19.9	217
23.2	39.2	229	60.0	20.0	226
13.0	40.6	215	40.1	30.0	199
27.8	20.3	322	50.1	30.0	210
16.5	64.0	142	39.9	40.0	184
19.3	49.4	149	50.2	40.0	195
40.7	10.7	331	30.0	50.1	153
35.6	17.9	301	40.9	50.0	170
19.0	54.3	141	30.0	60.0	131
31.0	10.7	371	20.0	70.0	168
9.8	79.0	247	60.0	30.0	217
9.3	71.7	210	70.0	20.0	230
27.2	33.8	219	80.0	10.0	241
18.8	19.8	373	40.0	20.0	266
22.1	48.7	146	30.0	40.0	163
2.9	70.2	215	20.0	60.0	127
16.2	50.9	142	10.0	80.0	248
3.5	56.6	149	25.1	50.0	147
25.4	30.9	267	25.0	62.0	120
11.4	26.1	362	24.0	60.4	125
11.4	31.2	338	20.0	62.0	124
8.4	49.2	146	22.4	60.1	128
50.0	9.8	283	20.0	65.0	139
60.0	10.0	230	22.8	62.9	124
26.4	61.8	124	27.0	61.0	126

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(3) Lehrman, Selditch and Skell, THIS JOURNAL, **58**, 1612 (1963).

(4) Briscoe, Evans and Robinson, *J. Chem. Soc.*, 1100 (1932).

calcium nitrate glasses were readily formed, and these showed no signs of further crystallization at room temperature even in the presence of large crystals of calcium nitrate. Cooling curves on melts of composition near that of the ternary eutectic showed a eutectic halt at 117.4°. No halt due to the inversion of potassium nitrate (128° in the pure substance[5]) was observed. This inversion of potassium nitrate should produce a slight break in the liquidus surface near the eutectic point.

The melting points of the ternary mixtures are given in Table II. The regions in which the three solid phases form (neglecting $4KNO_3 \cdot Ca(NO_3)_2$ and the low temperature form of potassium nitrate) and the eutectic points are shown in Fig. 2, the binary eutectics used being those of Rostkovsky[1f] and Carveth.[1a]

Summary

1. The liquidus curve of the binary system lithium nitrate–calcium nitrate has been determined. The eutectic temperature is 235.2°, the eutectic composition is at about 70% lithium nitrate.

2. The liquidus surface of the ternary system calcium, lithium and potassium nitrates has been explored partially. The ternary eutectic temperature is 117.4°, the eutectic composition is 15% calcium, 62% potassium and 23% lithium nitrates.

NEW YORK, N. Y. RECEIVED OCTOBER 15, 1936

[5] F. C. Kracek, *J. Phys. Chem.*, **34**, 225 (1930).

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Redetermination of the Deuterium–Protium Ratio in Normal Water

BY J. L. GABBARD AND MALCOLM DOLE

In the course of preparing some deuterium-free hydrogen for use in one of the researches on the isotopes of oxygen in progress in this Laboratory, it became possible to redetermine, by means of a method involving a knowledge of the oxygen isotope ratios in water and air, the deuterium–protium ratio in normal water. Limitations of space forbid a detailed discussion of the many previous measurements of this ratio; the reader is referred to the recent papers of Morita and Titani[1] and of Hall and Jones[2] for references and comments on earlier work. At present there seem to be three apparently accurate determinations of the deuterium–protium ratio in which the difficulties due to oxygen isotope fractionation on electrolysis were recognized and avoided, namely, those of Johnston ($-18.3\ \gamma$),[3] Morita and Titani ($-18.9\ \gamma$) and Hall and Jones ($-16.5\ \gamma$). The symbol γ represents in p. p. m. the density of deuterium-free water less the density of normal water; from the γ values the deuterium–protium ratio is calculated easily. The maximum difference in the above results ($2.4\ \gamma$) is greater than the experimental errors of density measurement and is due, we believe, to the different methods used by the above authors in bringing to normal or correcting for the oxygen isotope ratios in the waters under investigation.

Since the relative atomic weight of oxygen in air and in water has been determined recently[4] it is possible to solve the oxygen isotope problem by combining the deuterium-free hydrogen with oxygen of the air and after measuring the density of resulting water, the proper correction for the difference in the atomic weight of air and water oxygen can be applied, yielding what should be the correct density of water made of isotopically pure protium and the oxygen of normal water. From this latter value the D/H ratio in normal water is calculated readily.

Experimental

The electrolysis apparatus was very kindly constructed for us by Dr. P. W. Selwood who was able to give us frequently valuable advice and suggestions from his great store of electrolytic experience. The lengthy first and second fractionations were carried out by Mr. Stanley Cristol working under an NYA grant from the government. In the case of all electrolyses after the first two, sodium peroxide instead of sodium hydroxide was added to the water to make it conducting; sodium peroxide was used because it contains no deuterium, the excess oxygen was eliminated by boiling. Data for the preparation of deuterium-free water are given in Table I where the letters after the numbers are labels serving to distinguish and identify the various waters in order to clarify the table. All the different waters mentioned in this paper will be marked in this way so that the previous history of the water can be found readily by the reader (N signifies normal, or Lake Michigan, water).

Part of the water obtained from each electrolysis was decomposed electrolytically, the hydrogen passed over hot

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[1] N. Morita and T. Titani, *Bull. Chem. Soc. Japan*, **11**, 403 (1936).

[2] N. F. Hall and T. O. Jones, THIS JOURNAL, **58**, 1915 (1936).

[3] H. L. Johnston, *ibid.*, **57**, 484, 2737 (1935).

[4] M. Dole, *J. Chem. Phys.*, **4**, 268 (1936).

copper; it was next dried and then combined with dried atmospheric oxygen over a hot copper catalyst with the hydrogen always slightly in excess to prevent fractionation of the oxygen isotopes. The resulting water was condensed in a water condenser; in one experiment the water condenser was supplemented by a dry ice–acetone condenser, but no difference in the density of the water due to the introduction of the dry ice condenser could be detected. Data for the preparation of this water are given in Table II.

TABLE I

DATA OBTAINED IN THE PREPARATION OF DEUTERIUM-FREE WATER

Fractionation	Water taken, cc.	Water collected, cc.	% collected	Residue, cc.	Lost, cc.	cc. retained for hydrogen analyis
1	72,000 (N)	23,600 (A)	32.79	47,000	1400	
2	23,600 (A)	9,440 (B)	40.00			800 (B)
3	8,640 (B)	4,579 (C)	52.99	3,782 (D)	739	590 (C)
4	3,989 (C)	1,865 (E)	46.50	1,495 (F)	629	565 (E)
5	1,300 (E)	690 (F)	53.07	530 (G)	80	690 (F)

TABLE II

DATA OBTAINED IN THE PREPARATION OF WATER MADE FROM DEUTERIUM-FREE HYDROGEN AND ATMOSPHERIC OXYGEN

Fractionation	Water taken, cc.	Product, cc.	Residue, cc.	Water lost, cc.
2	800 (B)	300 (H)	200 (I)	300
3	590 (C)	285 (J)	50	265
4	500 (E)	255 (K)	50	195
5	675 (F)	440 (L)	50	185

The purification of the various waters and the method of measuring the density were essentially the same as previously described.[5]

In order to prevent the "light" water from being contaminated with normal water, some wash water for use in rinsing the various glass receptacles, thermometers, floats, etc., was prepared by electrolyzing approximately half of the residue from the second fraction in the hydrogen separation cells and combining the liberated hydrogen with atmospheric oxygen. Two liters of wash water having a density only slightly greater than the lightest fractions (J, K, L) were obtained.

The ordinary laboratory distilled water which comes originally from Lake Michigan was the standard water chosen. The hydrogen and oxygen of this water were assumed to be normal in their isotopic composition.

The density data are collected in Table III.

After the density of the various fractions had been measured, waters H, J, K, L, were mixed, the density of the mixture taken and then a very careful electrolytic fractionation carried out by decomposing 60% of the mixture. In this final step the air supplying the atmospheric oxygen was passed through a drying tower of solid potassium hydroxide and then through concentrated sulfuric acid.

The water resulting from the combustion of the electrolytic hydrogen and the atmospheric oxygen was completely recovered in a dry ice–acetone trap. These extra precautions did not lower the density of the "light" water below -9.0γ.

TABLE III

DATA FOR THE DENSITY OF THE VARIOUS WATERS

	Fraction no.	Label	Δt,°C	γ
	3	(J)	−0.029	− 8.7
			− .029	− 8.7
	4	(K)	− .029	− 8.7
			− .032	− 9.6
	5	(L)	− .030	− 9.0
			− .030	− 9.0
Accepted value:			− .030	− 9.0
2, 3, 4, 5 (Waters H, J, K, L, mixed):				
			− .029	− 8.7
2, 3, 4, 5 Mixed and further fractionated:				
			− .030	− 9.0
Water G			− .062	−18.6
Water M			− .041	−12.6

The density of water G was measured in order to see whether the electrodes of the cells had fractionated the oxygen isotopes during all the electrolyses. This water is probably equivalent to Johnston's light fraction from his second or third electrolysis since it represents the residue after decomposing 53% of water E from the fourth fractionation. The ability of the electrodes of the cells to fractionate the hydrogen isotopes was tested at the conclusion of the experiments; 1200 cc. of normal distilled water was placed in the cells and electrolyzed, and 490 cc. of first fraction water resulted. This water, water M, had a γ value of -12.6, which proved that the electrodes had not lost their activity for hydrogen isotope separation.

We conclude from our measurements that the density of deuterium-free water containing atmospheric oxygen is 9.0 p. p. m. lighter than purified Lake Michigan water.

The close agreement between the densities of waters J, K and L, indicates that the hydrogen must have been brought to a constant isotopic composition which we assume is practically pure protium.

Discussion of the Data and Comparison with Previous Results

In order to calculate from our value of $-9.0\ \gamma$ the density of D-free water containing normal oxygen, it is necessary to know the exact value for the difference in density of waters made of normal oxygen and atmospheric oxygen. This value has been determined carefully by a number of workers using an electrolytic method with rather excellent agreement considering the different techniques involved and the geographical location of the standard waters. In Table IV we have summarized recently published results.

Accepting $6.4\ \gamma$ as the excess density of water containing atmospheric oxygen, we can subtract this number from our datum of $-9.0\ \gamma$ to obtain $-15.4\ \gamma$ as the difference in density between deuterium-free water and normal water, the oxygen of both waters being isotopically identical. In Table V we have summarized all published re-

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(5) M. Dole, THIS JOURNAL, **58**, 580 (1936); *J. Chem. Phys.*, **2**, 337 (1934).

TABLE IV

DIFFERENCE IN DENSITY OF WATER CONTAINING NORMAL OXYGEN AND ATMOSPHERIC OXYGEN. (THE HYDROGEN HAVING THE SAME ISOTOPIC COMPOSITION IN EACH CASE)

Investigator	γ
Dole[4]	6.0
Greene and Voskuyl[a]	6.0
Hall and Johnston[b]	6.6
Morita and Titani[c]	7.0
Average	6.4

[a] C. H. Greene and R. J. Voskuyl, THIS JOURNAL, **58**, 693 (1936). [b] W. Heinlen Hall and H. L. Johnston, *ibid.*, **58**, 1920 (1936). [c] Ref. 1, p. 414.

sults for the γ-value of D-free water, and we have included also values of the D/H ratio (denominators rounded off to the nearest 100), calculated by the method of Morita and Titani,[1] using the accurate specific gravity value for heavy water given by Selwood, Taylor, Hipple and Bleakney.[6]

There is considerable discrepancy between these values for the D/H ratio. Christiansen, Crabtree and Laby,[7] Ingold, Ingold, Whitaker and Whytlaw-Gray,[8] and Tronstad, Nordhagen and Brun[9] do not state in their short "Letters to the Editor" whether or not they corrected for the electrolytic fractionation of the oxygen isotopes in their experiments. We are doubtful whether the D-free water prepared by Christiansen, Crabtree and Laby contained atmospheric oxygen as suggested by Morita and Titani,[1] inasmuch as the Australian workers stated that they burned the gases evolved. The data in Table V due to Edwards, Bell and Wolfenden,[10] and to Lewis and Macdonald[11] were obtained by measuring the rate at which deuterium concentrates on electrolysis. Knowing the fractionation factor for the cells, the D/H ratio in normal water can be calculated. Lewis and Macdonald made no attempt to correct for oxygen isotope fractionation. This method does not seem to be as accurate, however, as the method of measuring the density of D-free water.

TABLE V

DENSITY DIFFERENCES BETWEEN DEUTERIUM-FREE WATER AND NORMAL WATER FROM DIFFERENT INVESTIGATIONS

Investigation	Source of water	γ	D/H Ratio
This investigation	Lake Michigan	-15.4	1:6900
Christiansen, Crabtree and Laby	Melbourne rain water	-12.7	1:8400
Edwards, Bell and Wolfenden	Oxford, England		1:6200
Hall and Jones	Lake Mendota	-16.5	1:6500
Ingold, Ingold, Whitaker and Whytlaw-Gray	London, England	-12.0	1:8900
Johnston	Columbus, Ohio	-18.3	1:5800
Lewis and Macdonald	Berkeley, Calif.		1:6500
Morita and Titani	Osaka, Japan	-18.9	1:5600
Tronstad, Nordhagen and Brun	Rjukan, Norway	-18.5	1:5800

Johnston[3] assumes in his work that the oxygen isotope fractionation factor is independent of the kind of hydrogen isotope present in the water. This assumption was also tacitly made by one of us in obtaining the data of Table IV. Selwood, Taylor, Hipple and Bleakney[6] have calculated with the aid of the theory given by Eyring and Sherman[12] that the separation ratio for the bonds D-O^{18}, D-O^{16} is slightly higher than that for the bonds H-O^{18}, H-O^{16}, but they state that even when the concentration of deuterium had reached the high percentage of 90%, the effect was too small to be detected experimentally. Unless there are some unknown influences at work in the region of low deuterium concentration, it would appear that the assumption of independence for the oxygen isotope fractionation factor is entirely justified. Probably a greater source of uncertainty in Johnston's work is the difficulty regarding the extrapolation. We have reëxtrapolated his data, drawing our straight line through all of his circles, but purposely sloping the line to yield an extrapolated value as near our datum of $-15.4\ \gamma$ as possible. The result of this extrapolation was $-15.9\ \gamma$, which indicates that Johnston's results are not entirely inconsistent with the work of this paper. We are not insisting, however, that our extrapolation is as reliable or more reliable than his.

It is more difficult to explain the discrepancy between the result of this investigation and that of Morita and Titani, which seems to have been carried out very carefully.[1] It is possible, of course, that Japanese water may contain more deuterium than the water of Lake Michigan, but it seems hardly likely that the difference will be great enough to cause a difference of 3 p. p. m. in the density, particularly since one of us has re-

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(6) P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr., and W. Bleakney, THIS JOURNAL, **57**, 642 (1935).

(7) W. N. Christiansen, R. W. Crabtree and T. H. Laby, *Nature*, **135**, 870 (1935).

(8) E. H. Ingold, C. K. Ingold, H. Whitaker and R. Whytlaw-Gray, *ibid.*, **134**, 661 (1934).

(9) L. Tronstad, J. Nordhagen and J. Brun, *ibid.*, **136**, 515 (1935).

(10) A. J. Edwards, R. P. Bell and J. H. Wolfenden, *ibid.*, **135**, 793 (1935).

(11) G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.*, **1**, 341 (1933). These authors also used the method of measuring the density of D-free water in estimating their D/H ratio.

(12) H. Eyring and A. Sherman, *ibid.*, **1**, 345 (1933).

cently found no measurable difference in the deuterium content of fresh and salt water.[13]

Hall and Jones' datum of $-16.5\ \gamma$, which differs from ours by 1.1 p. p. m., was obtained in two ways although both methods involved the normalization of the oxygen in the water by equilibration with carbon dioxide gas which had been equilibrated previously with normal water. Since carbon dioxide comes so slowly to equilibrium with water and since the equilibrium constant is a function of temperature, it would seem that this method is undesirable and difficult of application. The assumption is also made that the oxygen isotope equilibrium between carbon dioxide and water is the same irrespective of the deuterium content of the water. We examine this assumption below. Hall and Jones in a second series of experiments burned their cell hydrogen with atmospheric oxygen obtaining results which varied considerably, although their last measurements ($-8.9\ \gamma$) agreed almost exactly with ours ($-9.0\ \gamma$). However, on equilibration with carbon dioxide this water which was apparently exactly like ours, changed in density to $-16.5\ \gamma$, whereas our calculated result is $-15.4\ \gamma$. Thus the discrepancy between the work of Hall and Jones and our own is seen to be due to the two different ways in correcting for the oxygen isotope ratio. We believe that our method which consists essentially in measuring the oxygen isotope ratio in atmospheric oxygen gives a more reliable result than the method of Hall and Jones based on the carbon dioxide equilibration.

Calculation of Some Isotopic Exchange Equilibrium Constants.—Among the equilibrium constants of isotopic exchange reactions which Urey and Greiff[14] have calculated from spectroscopic data and statistical theory constants involving D_2O^{16} and D_2O^{18} are missing, because, undoubtedly, the supply of heavy water is so limited that no practical importance is attached to these constants, but in order to answer certain theoretical questions which have arisen we decided to calculate the equilibrium constants of the oxygen isotope reactions between carbon dioxide, oxygen and heavy water. If the distribution function ratio[15] $f_{D_2O^{18}}/f_{D_2O^{16}}$ is known, then the desired equilibrium constants can be calculated easily, making use of other distribution function ratios tabulated by Urey and Greiff. Frequencies for the D_2O^{16} and D_2O^{18} molecules were calculated using the equations of Van Vleck and Cross[16] after their force constants k_1, k_{12} and k_3 had been adjusted to give agreement between the calculated frequencies of the D_2O^{16} molecule (2666.0, 2785.0, 1176.6) and those (2666, 2784, 1179) observed by Barker and Sleator.[17] The results of the calculation are collected in Table VI.[18]

TABLE VI

MOLECULAR CONSTANTS

Molecule	ω_1	ω_2	ω_3	A_2/A_1	B_2/B_1
D_2O^{16}	2666.0	2785.0	1176.6	1.0083	1.0229
D_2O^{18}	2646.8	2770.3	1169.5		

DISTRIBUTION FUNCTION RATIOS

	273.1°A.	298.1°A.	600°A.
$\frac{f_{D_2O^{18}}}{f_{D_2O^{16}}}$	1.3043	1.2926	1.2316

EQUILIBRIUM CONSTANTS AND ENRICHMENT FACTORS

Reaction	$K_{298.1°}$	Enrichment factor
$CO_2^{16} + 2D_2O^{18}(g) \rightleftharpoons CO_2^{18} + 2D_2O^{16}(g)$	1.065	1.032
$O_2^{16} + 2D_2O^{18}(g) \rightleftharpoons O_2^{18} + 2D_2O^{16}(g)$	0.9990	0.9995

The distribution function ratio, $f_{D_2O^{18}}/f_{D_2O^{16}}$, is about 3% greater than the ratio $f_{H_2O^{18}}/f_{H_2O^{16}}$; hence the equilibrium constants of the reactions listed in Table VI are about 6% smaller than the constants for the normal water equilibria. Thus O^{18} tends to concentrate less in the gas phase and more in the aqueous phase; in the case of the oxygen–water equilibrium the new calculations show that the equilibrium concentrations of the reaction are shifted far enough so that O^{18} concentrates in the heavy water rather than in the gas. However, the difference in behavior between the carbon dioxide–water equilibrium and the carbon dioxide–heavy water equilibrium is not great enough to invalidate the equilibration method of Hall and Jones. In regard to the relative rate at which the carbon dioxide comes into equilibrium with the two kinds of water, nothing is known at the present time.

Summary

Deuterium-free hydrogen has been prepared and combined with atmospheric oxygen yielding

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[13] M. Dole, *J. Chem. Phys.*, December, 1936.

[14] H. C. Urey and L. Greiff, THIS JOURNAL, **57**, 321 (1935).

[15] Urey and Greiff's nomenclature is used throughout this discussion.

[16] J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.*, **1**, 350, 357 (1933).

[17] E. F. Barker and W. W. Sleator, *ibid.*, **3**, 660 (1935).

[18] At the suggestion of the referee of this paper we give the values of the force constants calculated by us by arbitrarily setting the value of k_{13} at 0.05×10^5, and by solving simultaneously three independent equations, for k_1, k_{12} and k_3. These three equations were obtained by substituting known values for the a_{ij} constants into the three equations for λ_1^2, λ_2^2 and λ_3^2. These last three quantities were also known from the experimental data. The new values of the force constants for the D_2O^{16} molecule are k_1, 7.796×10^5; k_{12}, 0.4976×10^5; k_3, 0.3598×10^5; and k_{13} 0.05×10^5.

water lighter by 9 p. p. m. than Lake Michigan water. When 6.4 p. p. m. are added to 9 p. p. m. to correct for the difference in atomic weight of atmospheric oxygen and aqueous oxygen, the density of D-free water containing normal oxygen is 15.4 p. p. m. lighter than normal water. From this the ratio of deuterium atoms to hydrogen atoms in Lake Michigan water is calculated to be 1:6900. Our density value of $-15.4\ \gamma$ agrees within 1.1 p. p. m. with that of Hall and Jones, $-16.5\ \gamma$, and confirms their belief that the commonly accepted value for the D/H ratio is too high and should be revised downward. Our result indicates, however, that the downward revision should be somewhat more than that recommended by Hall and Jones.

Isotopic exchange equilibrium constants involving D_2O^{16} and D_2O^{18} have been calculated and tabulated.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 21, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Solubilities of Potassium Chloride in Deuterium Water and in Ordinary Water from 0 to 180°

BY R. W. SHEARMAN AND ALAN W. C. MENZIES

Published measurements of solubility of salts in deuterium water[1] hitherto have been limited to a few determinations near room temperature. The present work is one of a series of studies over a wide temperature range undertaken in the hope of gaining insight into portions of the general subject of aqueous solubility.

Method and Materials.—For all our experiments with deuterium water, and for most of those with ordinary water, the method used was that described by Menzies.[2] A few experiments requiring much ordinary water in relation to the quantity of solute were carried out by the older synthetic method, where each experiment demands a separate sealed tube. Our method of securing and measuring steady temperatures has already been described;[2] and it may be added that about one-half of the measurements were carried out in the jacketed air-oven referred to in the earlier publication.

The deuterium water was similar to that described elsewhere,[3] with a content of 98.2% D_2O. The relative density of this water compared to ordinary water at 25° was taken as 1.1059 for the purposes of conversion of measured volumes to masses. In order to apply the small correction for the weight of water vapor present in the gas phase, values of the vapor pressure of saturated solutions of potassium chloride were derived, by extrapolation when necessary, from the work of Leopold and Johnston;[4] and these pressure values could, with adequate approximation, be adapted to suit the case of deuterium water solutions from a knowledge of solubility and of the vapor pressures of deuterium water relative to that of ordinary water.[3]

Potassium chloride is easily obtained of highest purity, and we estimate the impurity of our sample, other than water, as less than five parts per 10,000. Water was removed by slow heating to incipient fusion.[5]

Manner of Stating Solubility.—The solubility of potassium chloride in common water is reported in moles of solute per 1000 g. of water (55.51 moles H_2O), conformably to the practice of "International Critical Tables." To secure a comparable statement of solubility in deuterium water, we state the number of moles of solute per 1111.7 g. of solvent, which is 55.51 moles of D_2O. To arrive at this value from experiments made with 98.2% D_2O, we first computed, from the weights of solvent and solute used, the molal solubility in 1109.7 g. of our sample, which is the weight containing 55.51 moles of mixed D_2O and H_2O. By comparing the value so found with the molal solubility in ordinary water, we were able, by a short linear extrapolation, to arrive at the solubility per 55.51 moles of pure D_2O.

Experimental Results.—For all but the lower temperature experiments the identical solute material, 0.4086 g. of potassium chloride, was employed with both solvents. The total weight of 98.2% deuterium water employed was 1.39 g., and this was completely recovered in its original purity. In the case of deuterium water, the ratio of mass of solute to solvent was reduced for a few of the lower temperature experiments by using a smaller weight of solute in the apparatus described; and, in the case of ordinary water, by increasing the amount of solvent in separate sealed-tube experiments.

Table I records the results observed in ordinary water in the first two columns and in deuterium water in the third and fourth columns.

These observations were graphed in the manner described previously,[2] and solubility values read off for round values of temperature, as recorded in Table II, where, in the fourth column a comparison is made with the solubility values found in "International Critical Tables."

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[1] *Cf.* Taylor, Caley and Eyring, THIS JOURNAL, **55**, 4334 (1933).

[2] Menzies, *ibid.*, **58**, 934 (1936).

[3] Miles and Menzies, *ibid.*, **58**, 1067 (1936).

[4] Leopold and Johnston, *ibid.*, **49**, 1974 (1927).

[5] *Cf.* Cohen and Blekkingh, *Proc. Acad. Sci. Amsterdam*, **38**, 843 (1935).

TABLE I

OBSERVED SOLUBILITY OF POTASSIUM CHLORIDE (74.55) IN ORDINARY WATER AND IN DEUTERIUM WATER

M_{H_2O}, M_{D_2O} = moles KCl in 55.51 moles H_2O, D_2O, respectively

Temp., °C.	M_{H_2O}	Temp., °C.	M_{D_2O}
7.5	4.08	5.3	3.44
18.2	4.56	12.5	3.80
21.2	4.64	20.4	4.23
28.5	4.94	24.7	4.37
58.6	6.04	47.8	5.31
62.7	6.18	71.4	6.20
96.0	7.32	98.7	7.21
127.1	8.41	133.0	8.39
147.2	9.16	150.5	9.02
175.6	10.12	177.4	10.11

Extrapolated values are in italics. The fifth column states the percentage of the solubility value in ordinary water by which that in deuterium water falls short.

TABLE II

SOLUBILITIES OF POTASSIUM CHLORIDE IN ORDINARY WATER AND IN DEUTERIUM WATER AT ROUNDED TEMPERATURES

M_{H_2O}, M_{D_2O} = moles KCl per 55.51 moles H_2O, D_2O, respectively

Temp., °C.	M_{H_2O}	% correction to "I. C. T." values	M_{D_2O}	100 × $(M_{H_2} - M_{D_2O})/M_{H_2O}$
0	*3.78*	+0.5	*3.16*	*16.4*
10	4.20	+ .2	3.68	12.4
20	4.61	.0	4.16	9.8
25	4.80	− .2	4.38	8.7
30	5.00	− 2	4.59	8.2
40	5.37	− .6	5.01	6.7
60	6.09	−1.0	5.79	4.9
80	6.80	−0.4	6.52	4.1
100	7.51	.0	7.25	3.5
120	8.21	+ .1	7.97	2.9
140	8.89	− .1	8.67	2.5
160	9.57	− .3	9.36	2.2
180	*10.24*	− .6	*10.06*	*1.8*

It will be seen from Table II that the solubility in ordinary water diverges most largely from the "I. C. T." values in the region near 60°. Since the latter values were compiled, new measurements have been made by Scott and Durham,[6] who report solubilities at 50.21, 67.91 and 92.23°. Their values, followed by our own in parentheses for these temperatures, are 5.73 (5.75), 6.35 (6.36) and 7.20 (7.24), respectively. The divergencies here are in the opposite direction from those of "I. C. T."

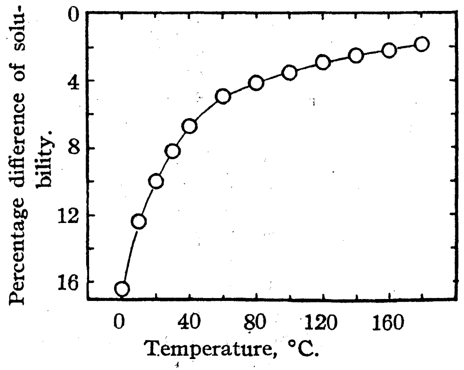

Fig. 1.—Comparison of solubility of potassium chloride in ordinary and in deuterium water.

The error in measurement by the method here used has been discussed elsewhere.[2] The average divergence of the experimentally determined points from our smooth curves was about 0.3% in the present work.

Graphical Comparison.—The diagram, Fig. 1, shows a plot of the values in Table II, column 5, against temperature.

Discussion.—The solubility of potassium chloride increases with temperature faster with deuterium water as solvent than with ordinary water. In addition to the nature of the solvent, another of the factors concerned in this is the heat of ion hydration. This in turn is influenced by the nature and the condition of the solvent.

Inspection of Fig. 1 makes it evident that, passing downward from 180 to about 60°, the change with temperature of the solubility difference is roughly rectilinear. From about 60° downward, the solubility difference increases at a much faster rate than before. This may perhaps be correlated with change with temperature of the average configurations in liquid water.[7] Recalling that the temperature of maximum density for deuterium water is 11.6° as compared with 4.0° for ordinary water, one is led to believe that the forms or structures present in water just above the melting point persist to higher temperatures in the case of deuterium water than of ordinary water.

Contrary to a prevalent belief,[8] in comparing deuterium water with ordinary water as a solvent for salts it must not be thought that the former is a poorer solvent under all circumstances, for such is not the case.[9] Because such facts must be taken into consideration, further discussion will find more appropriate place after the solubility results for other salts have been communicated.

Summary

Values for the solubility of potassium chloride in ordinary water and in deuterium water have been reported in the temperature range 0–180°. The differences in solubility have been briefly discussed.

PRINCETON, N. J. RECEIVED DECEMBER 7, 1936

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[6] Scott and Durham, *J. Phys. Chem.*, **34**, 1434 (1930).

[7] *Cf.* Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[8] *Cf.* Hall, Wentzel and Smith, THIS JOURNAL, **56**, 1822 (1934).

[9] *Cf.* Miles, Shearman and Menzies, *Nature*, **138**, 121 (1936).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Surface Tension of Solutions of Electrolytes as a Function of the Concentration. I. A Differential Method for Measuring Relative Surface Tension

BY GRINNELL JONES AND WENDELL A. RAY

Introduction

Most salts may be classified among the "capillary-inactive substances" which give solutions having a surface tension slightly greater than that of pure water and which are negatively adsorbed in the surface layer within the range of concentration hitherto investigated. Measurements by many early investigators have shown that the surface tension–concentration curves are approximately linear and that the slope and curvature are less influenced by the individuality and valence type of the salt than the corresponding curves for most other properties of solutions of electrolytes.

The first careful work on dilute solutions (less than 0.2 N) appears to have been done under the supervision of Heydweiller by two of his pupils, Gradenwitz and Kleine, who used the capillary rise method. Heydweiller has assembled and critically analyzed the data available up to 1910.[1]

If Quincke's law, which may be expressed $\sigma_c/\sigma_0 = 1 + kc$, were really valid, then $(\sigma_c - \sigma_0)/\sigma_0 c = k$ should be a constant independent of the concentration. Heydweiller found, however, that for many salts $(\sigma_c - \sigma_0)/\sigma_0 c$ decreases rather sharply with rising concentration in the dilute range (below 0.2 N), passes through a flat minimum, and then rises slowly for concentrated (above about 2 N) solutions. Heydweiller suggests that the attractive forces between adjacent ions of opposite charge will cause an increase in the surface tension. He says, "The effect of ions n the surface tension is to be ascribed in greatest art to the electrical forces of their charges."

Schwenker[2] has measured the surface tension of ill more dilute (0.015 N up to 0.15–0.18 N) lutions of lithium, sodium and potassium chloles at 0° by measuring the vertical force necesy to pull a horizontal wire out of the solution. s surface tension–concentration curves for se three salts are identical at the lower concentions within his experimental error and have the same downward curvature at low concentrations which Heydweiller found to be characteristic of solutions of electrolytes. Schwenker regards this characteristic behavior to be in accord with Lenard's theory that the surface layer of water at a water–air interface is electrically negatively charged and that there is a positively charged layer at a lower depth.[3]

Wagner,[4] and later Onsager and Samaras,[5] have applied the Debye–Hückel theory of interionic attraction to the problem and reached the conclusion that the electric forces between the ions must cause a deficiency of ions in the surface layer and an increase of the surface tension. They derived the following equation for dilute aqueous solutions of uni-univalent electrolytes

$$\sigma_c/\sigma_0 = 1 + \frac{79.517}{D\sigma_0} c \log \frac{1.143 \times 10^{-3}(DT)^3}{c} \qquad (1)$$

where D is the dielectric constant of water and T the absolute temperature. It should be noted that this equation contains no parameters which are selected to fit the data, and also that it contains no quantities which are dependent on the particular salt or ions present. This equation, therefore, predicts that all uni-univalent salts should give identical surface tension–concentration curves, at least through the range of concentrations for which the authors would claim that their equation is valid. The available experimental data show that in the relatively high concentrations for which reliable data are available the curves are approximately, but not exactly, identical. The Onsager–Samaras equation predicts that the limiting slope at zero concentration should be plus infinity and have a very sharp negative curvature in the extremely dilute range. Data at sufficiently low concentrations to test this conclusion are not available. According to this equation, within the experimentally accessible range the surface tension–concentration curve should have a gentle positive but decreasing slope, which is qualitatively in accord with the data. The equation predicts that the relative surface

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A. Gradenwitz, Diss., Breslau, 1902; *Physik. Z.*, **3**, 329,); A. Kleine, Diss., Munster, 1908; A. Heydweiller, *Ann. k*, [4] **33**, 145–185 (1910).

G. Schwenker, *ibid.*, [5] **11**, 525 (1931).

(3) P. Lenard, *ibid.*, [4] **47**, 463 (1915).

(4) Wagner, *Physik. Z.*, **25**, 474 (1924).

(5) L. Onsager and N. N. T. Samaras, *J. Chem. Phys.*, **2**, 528 (1934).

tension should reach a maximum at $c = 0.54$ with the low value of only 1.0033. The available data give no indication that there is a maximum in the surface tension curves near half normal, or at any other concentration, and values much above the computed maximum have been observed for many salts. It is, therefore, evident that there have been terms omitted in the derivation of this equation which become significant substantially below half normal. Although in the derivation of their equation Onsager and Samaras limited themselves to uni-univalent salts, the available data indicate that the influence of valence on the surface tension is much less than on most other properties of electrolytes.

The object of this investigation is to study the relative surface tension of solutions of electrolytes as a function of concentration and nature of the salt, with special attention to very dilute solutions. Since we are interested in the interpretation of the data from the point of view of the interionic attraction theory of Debye, we are interested primarily in the conditions after equilibrium between the thermal and electrical forces has been established. We, therefore, desire to measure the static rather than the dynamic surface tension. Since the surface tension of solutions of salts differs only slightly from that of pure water (less than 3% for normal solutions), a higher order of precision will be needed to secure significant results for dilute solutions than has hitherto been obtained with any of the methods. For the theoretical purposes which interest us an accurate knowledge of surface tension relative to that of pure water will suffice and absolute values are not needed. This simplifies the experimental problem greatly. The capillary rise method seemed to be the most promising. We undertook, therefore, to modify the technique of this method to make it a differential method of sufficient precision for our purposes.

A Differential Method of Determining the Surface Tension of Solutions Relative to that of the Pure Solvent

In its fundamentals the capillary rise method of determining the absolute surface tension of a liquid consists in measuring the vertical difference in height between a meniscus in a narrow cylindrical tube, whose radius is determined independently, and in a connecting tube which is so wide that it has a flat surface at the center, together with an independent determination of the density of the liquid. The surface tension is then computed from the equation

$$\sigma = \frac{rhg(D - \beta)}{2} \cos \theta \qquad (2)$$

where r is the radius of the narrow tube at the level of the meniscus, h is the capillary rise measured above a connecting free surface of infinite extent, g is the acceleration of gravity, D is the absolute density of the liquid, and β is the density of the gas phase (air plus water vapor) at the temperature and the barometric pressure prevailing when the experiment is made, and θ is the angle of contact. For water and aqueous solutions in glass or silica tubes θ is zero if the surfaces are really clean. An approximate value of the capillary rise is obtained by measuring the difference in elevation between the lowest points in the menisci in the narrow and wide tubes. The true capillary rise, h, is then obtained by applying a correction for the liquid in the upper and lower menisci by Rayleigh's[6] formula. When necessary, subscripts are used to distinguish between the capillary rise for a solution, h_c, and that of pure water, h_0.

The density can be determined easily within 0.001% and the value of the acceleration of gravity can be regarded as known, so that the accuracy of the result depends on the unavoidable experimental errors in determining r and h.

The radius of the capillary has usually been computed from measurements of the length of a weighed drop of mercury in the capillary. This requires the assumption that the capillary is a true right circular cylinder, whereas even the best capillary obtainable may be more or less elliptical and conical. Irregularities in the walls of the tube may cause optical distortion of the image and thus cause an error in the measurement. The capillary rise is found by measuring the elevation of the upper and lower meniscus on a vertical scale by means of a cathetometer. This reading on the meniscus in the capillary tube is comparatively easy, but it is much more difficult to obtain an accurate reading on the meniscus in the wide tube. The apparent readings are influenced by the adjustment of the illuminating device, the length of the focus, and the possible optical distortion of the image due to irregularities of the walls of the wide tube. Moreover, vibrations of the surface are apt to be disturbing.

Extreme care is required to reduce the combined effect of the errors in the radius and capillary rise to 0.1%, and it is doubtful if anyone has succeeded in reducing them below 0.05%.

We have devised a modification of the usual procedur
which makes it a differential method for measurements o
the surface tension of solutions relative to that of the pur
solvent and practically eliminates the two greatest sourc
of error in the older technique.

Errors due to deviation of the capillary tube from a tr
right circular cylinder and to inaccuracy in the determi
tion of the radius of the capillary are completely elimina
by bringing the meniscus of the solution and of pure wa
to the same part of the capillary tube, designated by a s
able permanent mark, and then determining the differe
in capillary rise in the wide tube.[7] By dividing the ex
sion for the surface tension of the solution, σ_c, by th
the pure solvent, σ_0, the radius of the capillary and
acceleration of gravity are eliminated entirely.

The difficulties of measuring the height of the me
in the wide tube by a cathetometer are avoided entir

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[6] Lord Rayleigh, *Proc. Roy. Soc.* (London), **A92**, 184 (1

[7] This device has been used by Gradenwitz and Kleine.

a modification of the procedure which permits the difference in capillary rise of solution and of solvent to be computed from data obtained by weighing.

The new differential capillarimeter is in principle suitable for any solvent, but up to the present time we have used it only with aqueous solutions and, since the properties of water influence or control some of the details, we shall in the following discussion assume that the solvent is water.

Derivation of the Equation for the Computation of the Relative Surface Tension of Solutions from the Experimental Data

The differential capillarimeter is shown in Fig. 1. It consists of a fine capillary tube of vitreous silica of radius r (r is 0.0136 cm. in our instrument) sealed to a wide tube which has been ground and polished internally to a true right circular cylinder of radius R (R is 2.1489 cm.). The empty instrument is weighed and then mounted vertically in a thermostat at 25.00°. Pure water is added to the instrument in an amount which will bring the meniscus in the capillary to the reference mark M. The volume of the water is then designated as V_0. The vertical height between the lowest point in the meniscus in the capillary and the lowest point of the meniscus in the wide tube is then measured by a cathetometer which, after applying two small meniscus corrections explained below, gives the true capillary rise for water, h_0. The instrument is then removed from the thermostat and weighed with its contents, which, after subtracting the weight of the empty instrument and adding the vacuum correction, gives the true weight of water W_0. Let D_0 represent the absolute density of water. It is obvious that $V_0 = W_0/D_0$.

Then the instrument is emptied, dried and remounted in the thermostat and filled with the proper amount of solution containing c gram equivalents of salt per liter to bring the meniscus in the capillary again to the mark, M. The capillary rise is $h_c = h_0 + \Delta h$. It is not necessary
determine h_c by making measurements with the
tometer and adding meniscus corrections,
this is sometimes done as a check. The
then removed from the thermostat,
nd weighed with its contents,
ng the weight of the empty
the vacuum correction,
lution W_c. The volume
volume of the solution
here D_c is the absolute
The density is determined independently in a suitable pycnometer. Then we may write

$$\sigma = \frac{\sigma_c}{\sigma_0} = \frac{rg\ (D_c - \beta_c)h_c}{rg\ (D_0 - \beta_0)h_0} = \frac{(D_c - \beta_c)(h_0 + \Delta h)}{(D_0 - \beta_0)h_0} = \frac{D_c - \beta_c}{D_0 - \beta_0} + \frac{(D_c - \beta_c)\Delta h}{(D_0 - \beta_0)h_0} \tag{3}$$

Since we bring the upper meniscus to the same part of the capillary for the solution and for water, the value of r cancels out and does not have to be known exactly.

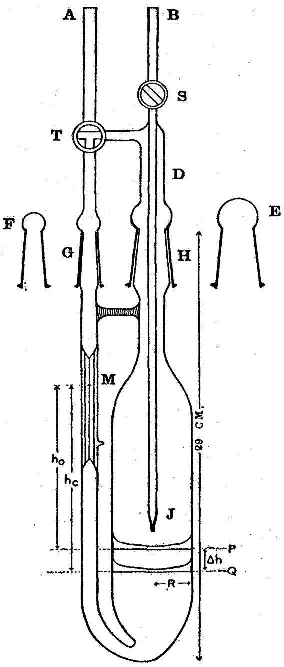

Fig. 1.—Silica capillarimeter.

Let W_0' and V_0' represent the weight and volume of water contained in the apparatus from the upper surface in the capillary to the level of a free surface of infinite extent which is assumed to be in hydrostatic equilibrium with the liquid in the instrument (P in the diagram), and let W_0'' and V_0'' represent the weight and volume between the meniscus in the wide tube and the level of the free surface (not the tangent to the lowest point of the meniscus). Then $W_0 = W_0' + W_0''$ and $V_0 = V_0' + V_0''$. The force of gravity on the liquid in the meniscus above the level of the free surface is balanced partly by the surface tension and partly by the buoyancy of the air. Therefore, we may write

$$W_0''g = D_0V_0''g = 2\pi R\sigma_0 + V_0''\beta_0 g \tag{4}$$

$$V_0'' = \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} \tag{5}$$

$$V_0' = V_0 - \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} = \frac{W_0}{D_0} - \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} \tag{6}$$

and in an exactly analogous manner we may write for the solution

$$V_c' = V_c - \frac{2\pi R\sigma_c}{g(D_c - \beta_c)} = \frac{W_c}{D_c} - \frac{2\pi R\sigma_c}{g(D_c - \beta_c)} \tag{7}$$

Since the wide tube is a true cylinder of radius, R, and is mounted vertically, we may write

$$\Delta V = V_0' - V' = \pi R^2 \Delta h \tag{8}$$

$$\Delta h = \frac{1}{\pi R^2}\left\{\frac{W_0}{D_0} - \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} - \frac{W_c}{D_c} + \frac{2\pi R\sigma_c}{g(D_c - \beta_c)}\right\} \tag{9}$$

Making this substitution in equation (3) gives

$$\sigma = \frac{\sigma_c}{\sigma_0} = \frac{D_c - \beta_c}{D_0 - \beta_0} + \frac{(D_c - \beta_c)}{(D_0 - \beta_0)}\frac{\Delta h}{h_0} = \frac{D_c - \beta_c}{D_0 - \beta_0} + \frac{(D_c - \beta_c)}{(D_0 - \beta_0)\,\pi R^2 h_0}\left\{\frac{W_0}{D_0} - \frac{2\pi R\sigma_0}{g(D_0 - \beta_c)} - \frac{W_c}{D_c} + \frac{2\pi R\sigma_c}{g(D_c - \beta_c)}\right\} \tag{10}$$

Then a purely algebraic and rigid transformation remembering that $r = 2\sigma_0/gh_0(D_0 - \beta_0)$ gives the equation

$$\sigma = \frac{\sigma_c}{\sigma_0} = \left\{\frac{D_c - \beta_c}{D_0 - \beta_0}\right\}\left\{1 + \frac{1}{\pi R^2 h_0 (1 - r/R)}\left(\frac{W_0}{D_0} - \frac{W_c}{D_c}\right)\right\} \tag{11}$$

It should be noted that this equation does not involve any assumption that the reservoir is so wide that the capillary rise in this tube is negligible, nor does it contain any assumption that the meniscus in the wide tube has the same shape for the solution and for water. If the derivation is carried through with these assumptions the result is the same, except that the factor $(1 - r/R)$ in the denominator of the second term is missing.

Precision Analysis

For the purpose of precision analysis it is more convenient to write equation (11) in the equivalent form

$$\sigma = \frac{\sigma_c}{\sigma_0} = \frac{D_c - \beta_c}{D_0 - \beta_0} + \frac{(D_c - \beta_c)}{(D_0 - \beta_0)}\frac{(W_0 D_c - W_c D_0)}{\pi R(R - r)h_0 D_0 D_c} \tag{12}$$

For all the cases reported below, the first term in equation (12), $(D_c - \beta_c)/(D_0 - \beta_0)$ is greater than 1 and less than 1.15. The second term is negative in all cases yet encountered and much smaller (the greatest numerical value so far experienced is 0.06338 for 3 N potassium chloride) and may, therefore, be regarded as a correcting term. It is, therefore, obvious that the accuracy of the final result will depend directly upon the accuracy of the determination of the densities of our solutions and that the quantities which are involved as factors of the second term do not have to be known with as great accuracy as the densities. Since in our instrument r/R is 0.00633, the final result will be very little influenced by an error in r.

D_0, β_c, β_0 and π may be regarded as known without significant error, but all of the other quantities appearing in the equation are determined by experiment and are subject to experimental errors which may influence the accuracy of the computed relative surface tension. From the principles of partial differentiation we may write

$$\Delta\sigma = \frac{\partial\sigma}{\partial D_c}\Delta D_c + \frac{\partial\sigma}{\partial W_0}\Delta W_0 + \frac{\partial\sigma}{\partial W_c}\Delta W_c + \frac{\partial\sigma}{\partial h_0}\Delta h_0 + \frac{\partial\sigma}{\partial R}\Delta R + \frac{\partial\sigma}{\partial r}\Delta r + \frac{\partial\sigma}{\partial T}\Delta T + \frac{\partial\sigma}{\partial(r_c/r_0)}\Delta\frac{(r_c)}{(r_0)} \tag{13}$$

Although equation (12) does not contain the temperature, T, explicitly, σ is a function of the temperature, and therefore to obtain a complete differential equation the term $\partial\sigma\Delta T/\partial T$ must be added. In the derivation of equation (12) it was assumed that the solution and water are brought to the same part of the capillary so that $r_c = r_0$. The error caused by a failure to meet this condition perfectly in the experiments is represented by the term $\partial\sigma\Delta(r_c/r_0)/\partial(r_c/r_0)$.

The problem now is to carry out the differentiation indicated in equation (13) and to substitute actual numerical data for each algebraic symbol in the total differential equation. In Table I we have used the data for three different solutions of potassium chloride selected to be typical of a dilute solution, an intermediate solution, and a very concentrated solution to compute the experimental errors in the measured quantities, D_c, W_0, W_c, h_0, R and r, which would each separately cause an error of 0.001% in the relative surface tension for an instrument for which h_0 = 10.834 cm., R = 2.1489 cm. and r = 0.0136 cm.

TABLE I

PRECISION ANALYSIS

	0.001 N KCl	0.1 N KCl	3 N KCl	
D_c	0.997116	1.001787	1.12808	G./ml.
W_0	84.9947	84.9947	84.9795	G.
W_c	85.0318	85.7047	106.1728	G.
D_c	+0.0000064	+0.0000064	+0.0000064	G./ml.
W_0	+ .00155	+ .00155	+ .00137	G.
W_c	− .00155	− .00155	− .00155	G.
h_0	+ .5	+ .055	+ .0038	Cm.
R	+ .05	+ .0054	+ .00017	Cm.
r	− .1	− .0108	− .00033	Cm

The foregoing table, interpreted in the our experience with the method, shows accuracy of the result will probably influenced by the errors in W_0 and W_c because it is difficult to determine them experimentally within 0.0015 g. It should, however, be noted that any systematic error in W_0 is likely to be duplicated in W_c and hence these errors are likely to compensate each other. The quantity D_c ranks next in its probable influence on the result because it is difficult to determine the density of a solution within 6 parts in a million, although by using large pycnometers (50 cc.) results can be duplicated within this limit. The combined effect of these errors should not exceed 0.003% with our apparatus. On the other hand, it is experimentally easy to determine h_0, R and r within the limits required of them except that for the most concentrated solutions the determination of R commences to become critical. The experimental error in R may be about 0.0001 cm. The radius of the capillary, r, is computed from the capillary rise with water, and the error in r depends mainly on the error in the value σ_0 selected from the literature for the calculation. An error of about 2.5% in the assumed value of σ_0 would be needed to cause an error of 0.00033 cm. in r and hence an error of 0.001% in the relative surface tension of a 3 N potassium chloride solution. Since σ_0 is probably known within 0.1%, errors due to r are insignificant in all the cases yet investigated.

The absolute surface tension of water at 25° changes 0.22% per degree, which would require that the temperature should be fixed within 0.0045° in order to fix the absolute surface tension within 0.001%. Since it is probable that the absolute surface tension of solutions varies with the temperature nearly the same as water, it follows that the temperature coefficient of the relative surface tension of solutions to that of water is presumably much smaller than the figure given above, so that a substantially greater error than 0.005° in our temperature scale could be tolerated. Since we had available a very good thermometer having a scale of 6 cm. per degree, which had been calibrated at the Bureau of Standards, we are confident that the working temperature of our thermostat was so near to 25.00° that no significant error is involved. A more dangerous source of error would be a variation of the temperature of the thermostat during the interval between the measurements on water and on the solutions. Our thermostat was good enough so that the maximum variation ever observed was safely within the tolerable limit of 0.004°.

The foregoing analysis also assumed that the radius of the tube is the same for the solution and for water. Since the position of the meniscus when the capillarimeter is filled may differ from the reference mark by ±0.001 cm., a variation of radius of 0.001% over a range of 0.002 cm. or 0.5% per cm. might cause an error of 0.001% in the relative surface tension. It is believed that our capillary is uniform within this tolerance (see page 192).

The advantages of our differential method over the old method are shown by a similar analysis of the formula

$$\sigma = \frac{\sigma_c}{\sigma_0} = \frac{g(D_c - \beta_c)h_c r_c}{g(D_0 - \beta_0)h_0 r_0}$$

On differentiating with respect to each of the experimentally determined quantities and substituting the numerical data for the 0.001, and 0.1 and 3 N potassium chloride solutions in this equation, it appears that the requirements for precision are nearly independent of the concentration and, therefore, a detailed table is omitted. These calculations show that an error of 0.000010 g./ml. in D_c, an error of 0.00011 cm. in either h_c or h_0 will each cause an error of 0.001% in the relative surface tension. Although D_c can be determined within this tolerance, the probable error in h_c and h_0 is many times the safe limit. By comparison with the table given above it will be noted that the new method is more dependent on errors in D_c than the old, but that is of minor importance because, if unlimited amounts of solutions are available, the densities can be determined with sufficient accuracy. On the other hand, the influence of errors in h_0 is reduced greatly in the new method, especially at low concentrations, and the necessity of determining h_c is eliminated. Moreover, the old method, in which no effort is made to bring the meniscus to exactly the same part of the capillary, requires the assumption that $r_c/r_0 =$ 1.00000 over the working range of the capillary which may amount to 2 cm., whereas the new method only requires that the radius of the capillary shall be constant within 0.001% over a range of only 0.002 cm.

The Capillarimeter and its Accessories.—The capillarimeter (Fig. 1) has graduation marks, 0.1 mm. apart, engraved on the capillary tube. A segment of this tube was ground off to give a flat polished strip and the marks were cut on this surface by the use of a fine diamond point operated by a dividing engine. These marks were so fine as to be invisible to the naked eye, but were correspondingly sharp when viewed under the microscope. They were not visible when the tube was immersed directly in the water of the thermostat; this was remedied by enclosing the capillary tube in another tube, the intervening space being filled with hydrogen for better thermal conductivity. The wide tube of the capillarimeter before fabrication was ground and polished inside and outside to true coaxial right circular cylinders in order to permit an accurately reproducible vertical mounting of the instrument and to avoid optical distortion. The external and internal diameters of this tube were measured with a micrometer before fabrication and found to be 5.0126 and 4.3004 cm., respectively, with a maximum variation at any place of ±0.00013 cm. After the construction of the complete instrument the external diameter was again measured by the micrometer and found to be unchanged within the working range.

A special holder, equipped with precision levels and leveling screws, was constructed which ensured that the capillarimeter could be mounted in a definite reproducible vertical position inside a water thermostat which was maintained at 25 ± 0.003°. The levels of the menisci were measured by observation through a window of optically plane glass by means of a special cathetometer, whose vertical scale was calibrated by comparison with a standard Invar scale provided with a Bureau of Standards certificate. To improve the definition of the menisci an adjustable blackened metal screen with horizontal slits as used by Richards and Coombs[8] was installed behind the menisci. A window of frosted glass in the back wall of the thermostat permitted adequate illumination.

The internal radius of the wide tube and of the capillary were determined after the construction of the instrument. The capillarimeter in its vertical mounting inside the thermostat was filled with sufficient water to bring the menisci within the working range. After waiting forty minutes for temperature equilibrium the heights of the menisci were measured. A weighed quantity of water of about 30 g. was then added and the measurements repeated. Three such independent determinations, covering approximately the same working range, gave as computed values of the radius of the wide tube 2.14882; 2.14892; and 2.14883; average 2.1489 cm. This figure is believed to be more reliable than the figure 2.1504 cm. obtained with a micrometer before the construction of the instrument.

As a result of many readings the observed or apparent capillary rise for water at 25° was taken as 10.8293 cm. between the lowest level of two menisci. This figure must be corrected[9] by +0.00453 cm. for the liquid in the upper meniscus; and by +0.00068 cm. for the elevation of the lowest part of the meniscus in the wide tube above the level of an infinite connecting surface; giving 10.8345 cm. as the true capillary rise. Hence the internal radius of the capillary at the point M (or more accurately at a level about 0.0045 cm. above M where the gas–liquid interface becomes vertical) is computed to be 0.01361 cm., by the use of equation (2), assuming[10] that $\sigma = 71.97$ for pure water at 25, and that at Cambridge the acceleration of gravity is 980.4.

Similar measurements, made at intervals along the capillary near the mark, M, show that the radius changes by 0.26% of itself per centimeter of length. If we always bring the water and solutions to be compared within 0.001 cm. of the mark, which is possible experimentally, the error in the relative surface tension due to conicality of the capillary tube would be less than 0.001%, which is negligible.

Purification of Materials and Preparation of Solutions.—The impurities most to be feared are capillary active substances, especially traces of grease and oils. Any relaxation in extreme care to maintain perfect cleanliness is apt to be followed promptly by erratic results. The capillarimeter, solution flasks, delivery tubes and all glassware were cleaned by exposure to a hot mixture of concentrated sulfuric and nitric acids, and finally thoroughly rinsed with water. This process was repeated whenever there was the slightest indication of imperfect drainage.

Richards and Carver[11] have published results indicating the effect of dissolved air is to lower the surface tension of water at 20° by about 0.03%. This difference, however, is about their limit of error and may not be significant. It seemed impractical to carry out all of our measurements *in vacuo*. Since we are interested in relative results and since the effect of dissolved air, if any, would probably be very nearly the same for solutions and for water, we decided to make all measurements on water and on solutions which were saturated with air.

The water used was freshly distilled conductivity water. It was collected in large bottles and shaken to saturate it with air, then blown by filtered compressed air through a sintered Jena Glass filter into a "water tower" which served as a storage reservoir. It was made of Pyrex, was 1 meter high, and 8 cm. in diameter. The water was stored here overnight to permit capillary active substances to rise to the surface and any dust particles to settle out. The water was then withdrawn when needed through a tube from the interior of the reservoir. The cock which controlled the outflow was ungreased and so well ground that no lubricant except water was needed. When water was withdrawn, suitable adapters were used to guide the water into the solution flasks or into other receptacles. The development of this device for protecting the water from capillary substances or dust greatly improved the reproducibility of the results.

The purest potassium chloride which could be purchased was recrystallized twice with centrifugal drainage and fused in platinum. A saturated solution of this salt gave no color with phenolphthalein. Potassium sulfate was prepared and tested in an exactly similar manner, except that it was not fused but was heated to redness in platinum. The cesium nitrate was made from the mineral pollucite by Professor Brainerd Mears and was a part of the same material already used for viscosity measurements in this Laboratory. Sucrose was obtained from "rock candy," since our previous experience showed that this variety contains less electrolyte than sucrose from any other source. The carefully selected crystals were then placed in platinum Gooch crucibles in a centrifuge

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(8) T. W. Richards and L. B. Coombs, THIS JOURNAL, **37**, 1656 (1915).

(9) These corrections were computed by the equations given by Lord Rayleigh. Lord Rayleigh, *Proc. Roy. Soc.* (London), **A92**, 184 (1916).

(10) "I. C. T.," Vol. IV, p. 447.

(11) T. W. Richards and E. K. Carver, THIS JOURNAL, **43**, 846 (1921).

and washed with conductivity water to rinse off the surface and then dried in a vacuum at a temperature of 50°. The electrical conductivity of solutions of this sucrose was so low as to prove that the electrolyte present as an impurity was less than 0.001% and, therefore, negligible for our purposes.

All solutions were prepared by the weight method with extreme care to prevent contamination by capillary active substances. All weighings were corrected to vacuum, and the concentration in gram molecules per liter at 25° computed by the aid of the density which was determined for each solution. The density determinations were made by the use of three Ostwald pycnometers of slightly more than 50 cc. capacity. The results obtained with these three instruments usually checked within five parts in a million.

Capillarimetric Procedure.—Comparative measurements were made on the solutions and on water with every detail of manipulation, except the addition of salt, and of measurement as nearly identical as possible. The capillarimeter was cleaned, weighed, and hung in the thermostat in the proper position and the height of the reference mark on the fixed vertical scale measured. After standing for several hours to permit capillary-active substances, if present, to come to the surface, slightly less than the required amount (about 85 cc.) of water (or solution) was transferred to the capillarimeter through a tube containing a sintered Pyrex filter. The water (or solution) was brought to 25.00° before making the transfer to avoid condensation in the upper part of the capillarimeter and suitable precautions taken to deliver the water (or solution) to the lower part of the capillarimeter without spattering and the delivery tube was withdrawn without touching the neck of the capillarimeter and thereby wetting it. The cross head filled with water (or solution) from S to J was then placed in position, as shown in Fig. 1. After waiting about thirty minutes for temperature control, the liquid was sucked up into the capillary by opening the cock, T, and applying gentle suction at A. The meniscus was allowed to fall until it reached its position of rest and then observed through the telescope. Water (or solution) was then added drop by drop from J until the meniscus, when falling, came to rest within 0.001 cm. of the reference mark. Then, after the proper quantity of water had been added, the level of the lowest point of the meniscus in the capillary with reference to the mark, M, and to the fixed scale was measured and recorded. Then the level of the lowest point of the meniscus in the center of the wide tube was measured with reference to the fixed scale. The cross head of the capillarimeter was then removed, replaced by the caps (F and E, Fig. 1), and the capillarimeter removed from the thermostat, carefully dried externally, and weighed on a large Troemner balance against a suitable counterpoise. The balance was sensitive to 0.1 mg. but the results were not reproducible better than 1–2 mg.

The entire operation was then repeated as exactly as possible, using a solution instead of water. The measurement of the actual capillary rise for the solution is not needed for the calculations of the results, and was sometimes omitted when pressed for time, but often made as a check.

It is well known that solid surfaces become coated with a greasy film when exposed to air for a short time.[12] In order to allow all traces of capillary active substances which might be introduced in this manner to rise to the surface, all of the solutions were made up in much larger quantities than were required for the measurements and allowed to stand undisturbed in closed flasks for from six to eighteen hours before use. Only the interior fractions taken from near the bottom were employed in the actual surface tension measurements.

In order to test the effectiveness of this method, three solutions of approximately 0.001 molar potassium sulfate were made up in three different ways. The first solution was prepared from a sample of salt which was weighed in a platinum boat, then ignited to a red heat and dissolved as soon as it had cooled; the second solution was prepared from a sample which was exposed to the laboratory air for twenty-four hours without a cover; while the third solution was prepared from a sample of salt which was deliberately contaminated with olive oil, by wetting the salt with a solution of olive oil in ethyl ether. The ether was allowed to evaporate leaving about 0.2 mg. of oil on the surface of the crystals. The surface of this solution was obviously greasy. Two determinations of relative surface tension were made on each of these solutions, the first after standing for six hours, and the second after standing for eighteen hours. The results are shown in the following table.

	Soln. I	Soln. II	Soln. III
6 hours old	0.99983	0.99986	0.99986
18 hours old	.99983	.99987	.99985

All three solutions had the same surface tension within the experimental error, which proves that the technique of withdrawing the solution from the interior was adequate to prevent errors due to accidental contamination of the salt by dust carrying capillary active substances.

Experimental Data

In order to illustrate the concordance which can be obtained with the new differential method the data are given in full for 0.05 N potassium chloride. Two different solutions were prepared, as shown in the upper part of Table III. This also shows the values for h_0 and W_0 determined on the same day and with the same reference mark. Each solution was used for two entirely independent experiments in the capillarimeter as is shown in the lower part of the table. The following figures were used in computing the results: $D_0 = 0.997074$; $\beta_c = \beta_0 = 0.00117$; $R = 2.1489$ cm.; $r = 0.013607$ cm.; $1 - r/R = 0.993671$.

In order to save space in printing the data are given in more abbreviated form in Tables III, IV and V. The figures for the relative surface tension are the averages of at least two independent experiments. The greatest deviation for any solution was only 0.005% and the average deviation was only 0.002%.

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[12] Lord Rayleigh, *Phil. Mag.*, [5] **33**, 220 (1892); I. Langmuir, *Trans. Faraday Soc.*, **15**, Part 3, 67 (1920).

TABLE II

INTERPRETATION OF EXPERIMENTAL DATA

KCl, g.	3.5366		3.5365	
Solution, g.	948.211		948.186	
D_c	0.999442		0.999434	
	.999442		.999432	
	.999447		.999438	
D_c average, g./ml.	.999444		.999435	
c, g.-mol./liter	.050000		.050000	
$(D_c - \beta_c)/(D_0 - \beta_0)$	1.002380		1.002371	
Apparent capillary rise for water	10.8281		10.8280	
Corr. upper meniscus	+ 0.00453		+ 0.00453	
Corr. lower meniscus	+ .00068		+ .00068	
h_0, cm.	10.8333		10.8332	
$\pi R^2h_0(1 - r/R)$	156.165		156.162	
Apparent weight water	84.9265		84.8946	
Corr. to reference mark	− 0.0029		+ 0.0290	
Vacuum correction	+ .0896		+ .0895	
W_0, g.	85.0132		85.0131	
Apparent weight solution	85.2755	85.2746	85.2869	85.2912
Corr. to reference mark	− 0.0029	− 0.0015	− 0.0145	− 0.0174
Vacuum correction	+ .0896	+ .0895	+ .0892	+ .0888
W_c, g.	85.3622	85.3626	85.3616	85.3626
Apparent cap. rise	10.8170	10.8180	10.8180	10.8179
Corr. upper meniscus	+ 0.00453	+ 0.00453	+ 0.00453	+ 0.00453
Corr. lower meniscus	+ .00068	.00068	.00068	.00068
h_c, cm.	10.8222	10.8232	10.8232	10.8231
$W_0/D_0 - W_c/D_c$	− 0.1470	− 0.1474	− 0.1473	− 0.1483
$(W_0/D_0 - W_c/D_c)/\pi R^2h_0(1 - r/R)$	− .000941	− .000944	− .000943	− .000959
σ_c/σ_0	1.001437	1.001434	1.001426	1.001410
Average		1.00143		

TABLE III

RELATIVE SURFACE TENSION OF POTASSIUM CHLORIDE SOLUTIONS AT 25°

c	D_c	σ_c/σ_0	$(\sigma_c-\sigma_0)/c\sigma_0$
0.000100	0.997078	0.99997	−0.3
.000200	.997081	.99995	− .3
.000500	.997094	.99983	− .32
.001000	.997117	.99982	− .18
.002000	.997161	.99988	− .06
.005000	.997306	.99998	− .04
.010000	.997540	1.00013	+ .013
.020000	.998018	1.00047	+ .023
.050000	.999440	1.00143	+ .0286
.10000	1.001787	1.00273	+ .0273
.20000	1.006456	1.00514	+ .0257
.50000	1.020275	1.01197	+ .02354
.99996	1.042865	1.02299	+ .02299
1.99908	1.086749	1.04531	+ .02266
2.99647	1.129252	1.06894	+ .03453

TABLE IV

RELATIVE SURFACE TENSION OF POTASSIUM SULFATE SOLUTIONS AT 25°

c	D_c	σ_c/σ_0	$(\sigma_c - \sigma_0)/c\sigma_c$
0.000200	0.997088	0.99995	−0.25
.000400	.997100	.99991	− .20
.001000	.997140	.99988	− .12
.002000	.997202	.99982	− .09
.004000	.997349	.99993	− .018
.010000	.997773	1.00019	+ .019
.020000	.998478	1.00058	+ .029
.040000	.999880	1.00110	+ .0275
.10000	1.004043	1.00262	+ .0262
.19993	1.010886	1.00460	+ .0230
.40015	1.024412	1.00850	+ .0212
1.00142	1.063920	1.01956	+ .0195

TABLE V

RELATIVE SURFACE TENSION OF CESIUM NITRATE SOLUTIONS AT 25°

c	D_c	σ_c/σ_0	$(\sigma_c - \sigma_0)/c\sigma_c$
0.000100	0.997088	0.99992	−0.8
.000200	.997101	.99990	− .5
.000500	.997138	.99986	− .28
.001000	.997212	.99983	− .17
.002000	.997361	.99986	− .07
.005000	.997791	.99996	− .008
.010000	.998509	1.00013	+ .013
.020000	.999944	1.00046	+ .023
.050000	1.004258	1.00118	+ .0236
.10001	1.011430	1.00217	+ .0217

Interpretation of the Data

The densities of these three salts can be expressed over the entire range studied by equations having the form suggested by Root.[13]

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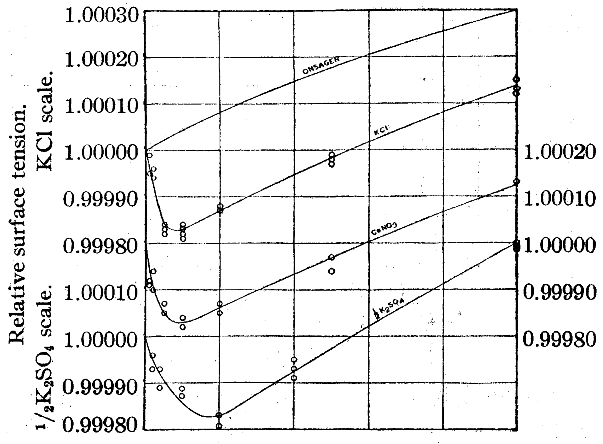
(13) W. C. Root, THIS JOURNAL, 55, 850 (1933).

For KCl: $d^{25}{}_4 = 0.997074 + 0.0480688c - 0.002283c^{3/2}$
For K_2SO_4: $d^{25}{}_4 = 0.997074 + 0.070994c - 0.004240c^{3/2}$
For $CsNO_3$: $d^{25}{}_4 = 0.997074 + 0.143708c - 0.000477c^{3/2}$

These equations agree with our data over the entire range studied and with the average deviations of less than 0.001%. This confirms previous experience in this Laboratory as to the usefulness of the Root equation.



Concentration.

Fig. 2.

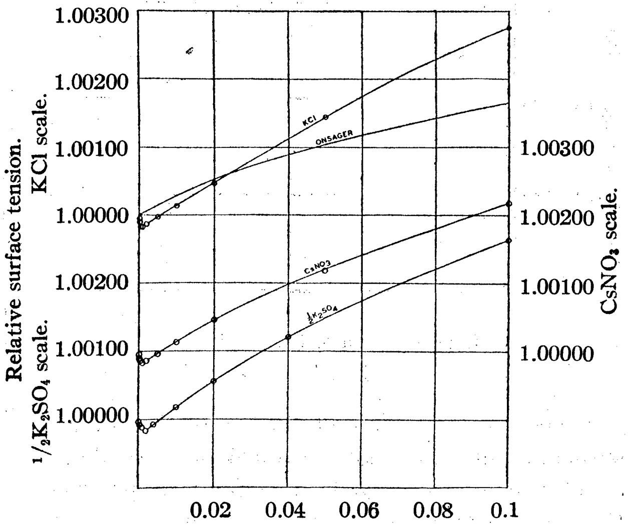
Within the ranges of concentration which have been studied by earlier experimenters, our data on the relative surface tension show the characteristics which Heydweiller has found to be typical of solutions of strong electrolytes; namely, $\sigma - c$ curves which are approximately linear with a gentle positive slope, but with a slight downward curvature which is especially pronounced in the dilute range (below 0.1 N), followed by an upward curvature in concentrated solutions (above 2 N) (see Figs. 3, 4 and 5). A comparison of the last column in our tables with the corresponding figures in the papers by Heydweiller and of Schwenker shows a marked similarity.

The most interesting and novel result of these measurements is that at extreme dilutions (less than about 0.006 N) the solutions of the three salts studied have a smaller surface tension than pure water, although above this lower limit the surface tension is greater than that of pure water and the surface tension–concentration curves show that these salts may be regarded as typical "capillary-inactive" substances.

The minimum surface tension which has been observed is not quite 0.02% less than that of pure water and occurs at about 0.001 N. In spite of the fact that the observed decrease is so small we believe that it is real and not due to experimental error. Figure 2 shows graphically the results of the separate experiments. Their averages only are given in the tables of numerical data. The concordance of the separate data, together with the precision analysis given above, make it seem probable that the error in the average for any concentration is not more than 0.002%. At the minimum in the surface tension the depression is, therefore, about nine times the probable error in the data. Moreover, the data give smooth curves which are similar for the three salts.

If the observed depression in surface tension is real, it follows from the well-known Gibbs theorem that at extreme dilutions these salts must be positively adsorbed in the surface layer, whereas above some lower limit of concentration (from 0.001 to 0.002 normal) there must be a deficiency in the surface layer or negative adsorption.

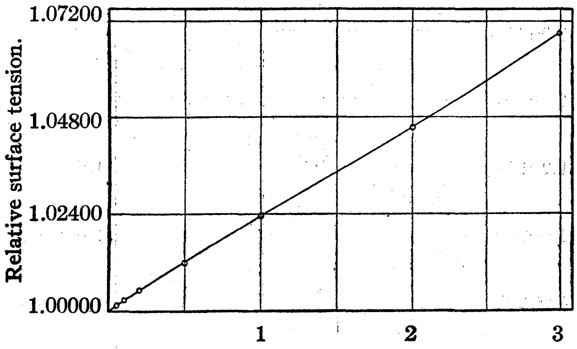
It would, of course, be premature to generalize from observations on three salts only that all salts will cause a diminution in surface tension and be positively adsorbed in the surface layer at sufficiently low concentrations. We intend to extend the experimental investigation to other salts of varied valence types and to study the influence of variations in the temperature and solvent. Since, however, the only three salts studied give similar curves, we shall assume tentatively that the phenomenon is general for aqueous solutions and discuss its implications on this assumption.



Concentration.

Fig. 3.

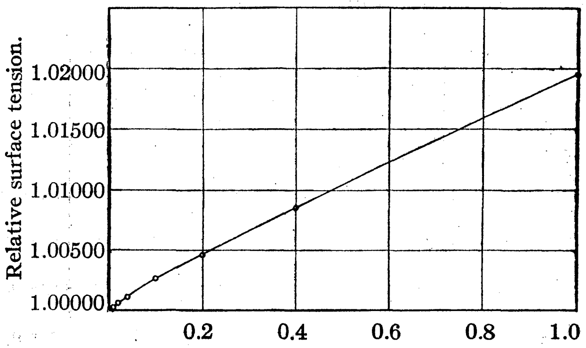
So far as we know this depression of the surface tension and positive adsorption at low concentrations has never been observed at a liquid–gas interface for any salt which gives increased surface tension at moderate concentrations and, therefore, can be classed as a "capillary-inactive" substance in the sense that this term has been used in the literature. An analogous phenomenon, however, has been observed at the interface between aqueous solutions of salts and organic liquids. Eversole and Dedrich, and Dedrich and Hanson,[14] who used a drop weight method, have measured the effect of sodium formate and of sodium acetate on the interfacial tension between aqueous solutions of these salts and mineral oil, or toluene, or benzene. They found a minimum in the curves for all of the cases studied, except for sodium acetate solutions against mineral oil. In the case of sodium formate solutions the minimum was found at high concentrations (above 1 *N*). The minimum for the sodium acetate solutions was not located very definitely, but was evidently much lower and was placed by the authors at around 0.1 to 0.15 *N*. "An attempt to explain the effect of these salts has been made on the basis of the Langmuir theory of molecular orientation and the increased interionic attraction in the interface due to the dielectric constant gradient in the interfacial layer."



Concentration of KCl at 25°.

Fig. 4.

McTaggart[15] has found that a bubble of air suspended in water moves toward the cathode in an electric field, which he interprets as proving that the surface film of water at the water–air interface is negatively charged. Lenard and his students[16] have reached the same conclusion from experiments on electrical effects in waterfalls and sprays. McTaggart then finds that by the addition of minute traces of salts containing positive ions of high valency (aluminum nitrate, lanthanum nitrate, thorium nitrate) to the water the air bubble will then move cataphoretically to the anode.



Concentration, $^1/_2K_2SO_4$ at 25°.

Fig. 5.

Freundlich, in a discussion of McTaggart's experiments on the cataphoresis of air bubbles says, "The fact that inorganic salts must here be assumed to be positively adsorbed does not appear to be in agreement with earlier experience. At all other interfaces, such as those of charcoal, glass, and oil, this assumption is justified, since they are actually positively adsorbed and lower the interfacial tension. At the interface water–air, however, they almost always raise the surface tension, and hence should be negatively adsorbed. This rise of σ refers, of course, to much more concentrated solutions. In such dilutions as come into question here a change in the surface tension cannot be established. It is not impossible that in this range of concentration the surface tension may be lowered by these electrolytes and positive adsorption take place, in accordance with the very general experience, that the first small amount of a foreign substance always causes a lowering of σ. The first gentle rise of the σ, c curve for inorganic salt solutions would thus be in the region of a minimum in the σ, c curve, only that this minimum, since it is very slight, cannot be measured."[17]

McTaggart's demonstration, however, that a trace of a salt containing a trivalent or tetravalent positive ion causes an air bubble to move to the anode merely proves that the surface film

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(14) W. G. Eversole and D. S. Dedrich, *J. Phys. Chem.*, **37**, 1205 (1933); D. S. Dedrich and M. H. Hanson, *ibid.*, **37**, 1215 (1933).

(15) H. A. McTaggart, *Phil. Mag.*, [5] **27**, 297 (1914).

(16) P. Lenard, *Ann. Physik*, [4] **47**, 463 (1915); W. Obolensky, *ibid.*, [4] **39**, 961 (1912); W. Busse, *ibid.*, [4] **76**, 493 (1925); A. Bühl, *ibid.*, [4] **83**, 1207 (1927); [4] **84**, 211 (1927); [4] **87**, 877 (1928).

(17) H. Freundlich, "Colloid and Capillary Chemistry," Methuen Co., London, 1926, pp. 75 and 279–280.

becomes positively charged. It does not necessarily prove that the salt as a whole, or even the positive ion, is positively adsorbed in the surface. There might be a deficiency of both ions in the surface layer (negative adsorption and increased surface tension), but if there were a partial separation of the ions in the process with the negative ion being drawn into the interior more than the positive ion, there would be established an electrostatic double layer which would account for McTaggart's results.

It next became of interest to determine whether the observed decrease in surface tension at great dilutions is caused by ions only, or whether it will also be found in dilute solutions of non-electrolytes which are capillary inactive in the sense that they give a slight increase in surface tension and are not adsorbed in the surface at moderate concentrations. Sucrose is known to cause a linear increase in surface tension within the lower part of the range of concentration hitherto investigated, but accurate measurements at extreme dilution are not available. We, therefore, made measurements on sucrose solutions from 0.0002 to 0.005 molar, as shown below.

TABLE VI

RELATIVE SURFACE TENSION OF SUCROSE SOLUTIONS AT 25°

c	D_c	σ_c/σ_0
0.000200	0.997093	0.99999
.000500	.997132	1.00002
.001000	.997202	1.00004
.002000	.997329	1.00008
.005000	.997726	1.00016

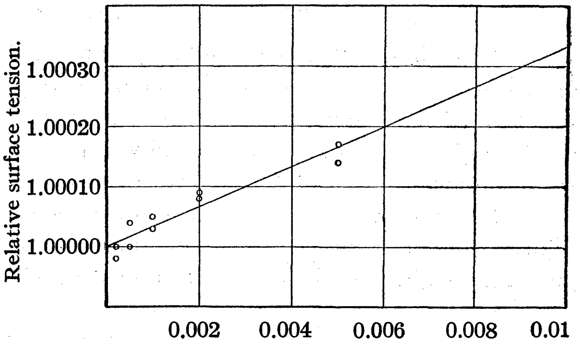
These results are shown in Fig. 6.

The slight indicated decrease at 0.0002 molar is within the limit of experimental error and is not significant. The data show a linear increase in surface tension and, therefore, show that sucrose is negatively adsorbed even at these extreme dilutions. It seems probable, therefore, that the influence which causes the decrease in surface tension and positive adsorption for salts is dependent on the electric charges of the ions.

Our results on the surface tension of salts are not in accord with the Onsager and Samaras equation, especially as to the sign of the limiting slope at infinite dilution. The Onsager–Samaras equation predicts that the limiting slope should be plus infinity, whereas the data show a large negative slope at extreme dilutions. The systematic differences between the data and the equation are shown in Figs. 2 and 3. The experimental and theoretical curves cross each other and there is no maximum in the experimental curve.

An inspection of our curves indicates that the influence which causes the diminution of surface tension is of such a nature that it reaches a limiting or saturation value at an extremely low concentration (perhaps under 0.002 N) and is maintained, but not appreciably increased, at higher concentrations.

The effect of the interionic attraction which is treated by Onsager and Samaras and which causes an increase in surface tension is of minor importance in the dilute range but increases approximately linearly with the concentration and becomes dominant above about 0.006 N.



Concentration of sucrose at 25°.

Fig. 6.

Onsager and Samaras in the derivation of their equation consider only the electric forces between the ions, but they do not consider the electric forces between the ions and the water molecules considered as electric dipoles. The electric forces between the dipolar water molecules must tend to maintain a systematic or ordered arrangement. A fairly detailed theory as to the nature of this ordered arrangement has been worked out by Bernal and Fowler.[18] If we add a salt to water in such great dilution that the interionic forces are negligible, there must nevertheless be a disturbance of the normal arrangement of the water molecules in the vicinity of the ions. The electric forces between the water dipoles would oppose this disturbance and tend to thrust the disturbing ions out into the surface, thus causing positive adsorption. In view of the electrically unsymmetrical character of the water molecules, this force may well be different for positive and negative ions, thus accounting for the effects described

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(18) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

by McTaggart and by Lenard and his students. Since the cohesion, and therefore also the surface tension, of water is probably largely due to the electric forces between the dipoles, a disturbance of the normal electric distribution may cause a diminution of the surface tension.

As the solution becomes more concentrated (about 0.01 N or above), the mutual attraction between ions of opposite polarity becomes stronger than the forces between the ions and the water molecules and causes negative adsorption and an increase in surface tension in the manner discussed by Onsager and Samaras. We may conclude, therefore, that the treatment of Onsager and Samaras is over simplified and thus fails to give a complete and accurate result.

Summary

1. A modification of the capillary rise method of measuring the surface tension of solutions relative to that of the pure solvent, which makes it a differential method and substantially improves the accuracy of the results, is described.

2. The relative surface tension of aqueous solutions of potassium chloride, potassium sulfate, and cesium nitrates has been determined at 25° from 0.0001 N up to 3, 1 and 0.1 N, respectively, and of sucrose solutions from 0.0002 molar up to 0.005 molar.

3. These three salts all increase the surface tension of water from 0.01 N up to the highest concentration studied and give surface tension–concentration curves which are typical of strong electrolytes that are capillary inactive and negatively adsorbed in the surface layer.

4. At extreme dilutions (below about 0.006 N) all three salts cause a decrease in surface tension and are, therefore, positively adsorbed in the surface layer at concentrations below that giving the minimum (about 0.001 N) of the surface tension.

5. Sucrose gives a linear surface tension–concentration curve with no change in the sign of the slope at extreme dilutions.

6. The data are not in accord with the Onsager–Samaras equation for the surface tension as a function of the concentration.

7. The influence which causes diminished surface tension and positive adsorption at extreme dilution is ionic in character and probably due to an interaction between the ions and polarized water molecules.

Cambridge, Mass. Received July 29, 1936

[Contribution from the Chemical Laboratory of Duke University]

The Action of Elementary Fluorine upon Organic Compounds. III. The Vapor Phase Fluorination of Hexachloroethane

By William T. Miller, Jr., John D. Calfee and Lucius A. Bigelow

Previous papers in this series[1] have described the fluorination of certain organic compounds dissolved in carbon tetrachloride, using, however, an open type of generator as the source of the halogen. This earlier procedure had two disadvantages, since the fluorine produced was contaminated with other gases, and also reacted to a considerable extent with the solvent. More recently, we have designed a new closed generator[2] capable of delivering fluorine 94–99% pure, and in addition have considered it desirable to avoid the use of solvents altogether. The present paper describes the vapor phase fluorination of hexachloroethane over a copper gauze catalyst. It is probable, of course, that the reaction took place at the surface of the metal, which acquired a thin coating of copper salts during the process, and cupric fluoride may have been the immediate fluorinating agent. However, the change did not occur rapidly at ordinary temperatures, and the gauze was not greatly attacked over a considerable period of time, even when heated. So far as the writers are aware, no similar, direct, vapor phase fluorination of an organic compound containing more than one carbon atom has as yet been reported, in which definite chemical individuals have been formed.

The procedure employed in this fluorination was exceedingly simple. The sample was placed in a horizontal tube, between two copper gauze rolls, suitably heated. The fluorine, diluted with nitrogen, was introduced at the center of one of

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[1] This Journal, 55, 4614 (1933); 56, 2773 (1934).

[2] Miller and Bigelow, *ibid.*, 58, 1985 (1936).

these rolls, in a manner somewhat similar to that described by Fredenhagen and Cadenbach.[3] Under appropriate conditions, a perfectly quiet, continuous reaction occurred, and the products were condensed at reduced temperatures. After purification and rectification in a Podbielniak still, the main product, which was *sym*-difluorotetrachloroethane, boiled at 92°, and melted at 24–25°, corresponding closely to the values previously reported by Locke, Bride and Henne,[4] who obtained the compound by another method. The yield of the pure haloethane was approximately 20%. A further study of this and similar reactions is contemplated.

Experimental

The fluorination was carried out in a Pyrex glass tube, diameter 2.8 cm., length 75 cm. The gas was introduced through a 6.3-mm. copper tube, closed at the end, but perforated irregularly along the last 4 cm. of its length. The perforations were surrounded by a tight roll of clean 20-mesh copper gauze, 6 cm. in length, which fitted snugly into the glass tube. The charge was placed in the 10-cm. space immediately following the gauze, and the total distance occupied by both of these was surrounded, on the outside, by a sliding metal air bath. Beyond the charge, the reaction tube was filled for a length of 25 cm. with another roll of gauze, surrounded by a second, independent air-bath. In this very simple set up, connections were made with ordinary stoppers, wrapped with copper foil and painted with Ceresin wax.

In operation, the tube was first swept out with nitrogen, and the second gauze heated to 160°. Then the fluorine, diluted with nitrogen in the ratio of 1:1.6, was passed in at a rate corresponding to a current of 3.8 amp. through the generator (roughly 1.5 liters per hour). Finally the first gauze was heated gradually to 125°, when a continuous reaction took place, the fluorine being always in excess. The products were condensed as a mixture of liquid and solid in a trap at about −40°. On warming to room temperature there remained a clear liquid, which was formed at the rate of about 1.6 g. per hour. For each 10 g. of hexachloroethane utilized, approximately 7.4 g. of this liquid was produced. The crude material was dissolved in ether, washed with 5% sodium carbonate solution and dried over calcium chloride, during which process a considerable portion of it dissolved. The ether solution was then fractionated directly in a Podbielniak still. The pure product, b. p. 92°, m. p. 24–25°, was obtained in approximately 20% yield. According to Locke, Bride and Henne[4] *sym*-difluorotetrachloroethane boils at 92.8° and melts at 24.7°.

Anal. Calcd. for $C_2F_2Cl_4$: F, 18.6; Cl, 69.6; mol. wt., 204. Found: F, 18.5, 18.7; Cl, 69.3, 69.5; mol. wt., 209, 210.

The fluorine analyses were made by the Willard and Winter method, after decomposing the sample in a Parr bomb.

When tetrachloroethylene, b. p. 119°, was fluorinated in a similar manner, with both gauzes at 130°, and the haloethylene in excess, *sym*-difluorotetrachloroethane, boiling at 92°, was also produced, in about 20% yield, and further identified by means of a mixed melting point. Considerable substitution took place at the same time, however. In this case, the sample was introduced by passing nitrogen through the refluxing liquid, heated in a bath at 135°.

Summary

Hexachloroethane has been fluorinated directly, in the vapor phase over a copper gauze catalyst. A 20% yield of pure *sym*-difluorotetrachloroethane was obtained. Tetrachloroethylene, under similar conditions, yielded the same product.

DURHAM, N. C. RECEIVED NOVEMBER 7, 1936

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(3) Fredenhagen and Cadenbach, *Ber.*, **67**, 928 (1934).

(4) Locke, Bride and Henne, THIS JOURNAL, **56**, 1726 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

The Action of Formaldehyde upon Cysteine

BY SARAH RATNER[1] AND H. T. CLARKE

The reaction of mercaptans with carbonyl compounds has received extensive study, but little attention has, until recently, been paid to the case of cysteine. In a study of the effect of formaldehyde on the titration curves of amino acids, Birch and Harris[2] observed, on the addition of formaldehyde to cysteine, the disappearance of the buffering action typical of the sulfhydryl group. Shinohara[3] in an investigation of the action of cysteine upon phosphotungstic acid, noted that the reducing power is inhibited completely by addition of formaldehyde. During the progress of the present investigation, Schubert[4] has described the formation of compounds of cysteine with various aldehydes, among them formaldehyde, and has produced evidence that the latter reacts with cysteine to form a thiazolidinecarboxylic acid. The present report covers a more extended investigation of this compound, its reactions, and its manner of formation.

The reaction between formaldehyde and cysteine can take place over a wide range of hydrogen ion activity. The product, which is remarkably stable toward both acid and alkali, possesses amphoteric properties, as is shown by the titration curve (Fig. 3). The empirical formula, $C_4H_7O_2NS$, and the conditions of formation indicate that the compound is formed from equimolecular quantities of cysteine and formaldehyde; its simple molecular character is indicated by the observed molecular weight of the methyl ester.

The nitrogen exists in the form of a secondary amino group, as is shown by the formation of an acetyl derivative and by the behavior with nitrous acid in the Van Slyke procedure.[5] The product, moreover, displays no tendency to racemize when its sodium salt is treated with acetic anhydride by the method of du Vigneaud and Meyer[6]—a result characteristic of secondary, in contrast to primary, α-amino acids.

The sulfur is present as a thio ether, for the nitroprusside reaction is negative; oxidation of the acetyl derivative by hydrogen peroxide leads, according to the conditions, to a sulfoxide or a sulfone. The unsubstituted acid, on treatment with hydrogen peroxide or iodine, is converted, with loss of formaldehyde, into cystine; with bromine water, cysteic acid is produced.

Among the compounds described by Schubert[4] some are formed by addition and others by condensation. It therefore seems probable that the reaction of cysteine with formaldehyde occurs in two steps, firstly, addition of the aldehyde, and secondly, ring closure by removal of a molecule of water. The formaldehyde may, theoretically, react primarily with either the sulfhydryl or the amino group of cysteine. A decision between these alternative possibilities can be reached by noting the ease of reaction of formaldehyde with acetylcysteine on the one hand, and S-ethylcysteine on the other. Experiment shows that the rotation of S-ethylcysteine at *p*H 5.12[7] is not changed by the presence of formaldehyde, while that of acetylcysteine is. At this *p*H, the rate of change is extremely rapid, both with cysteine and with acetylcysteine, but can be measured at higher hydrogen ion concentrations (*p*H 1–4). With cysteine (Fig. 1) the rotation reaches the theoretical value; with acetylcysteine (Fig. 2), on the other hand, the levo-rotation is distinctly lower than that observed for pure acetylthiazolidinecarboxylic acid under the same conditions. This may be interpreted as indicating the formation of a less strongly levorotatory addition compound of the type $RSCH_2OH$. By analogy, the first stage in the reaction between cysteine and formaldehyde may be regarded as taking place at the sulfur atom.

In determining the rates of the reaction at different *p*H levels, advantage was taken of the small optical rotation of cysteine and the conveniently large one of thiazolidinecarboxylic acid by follow-

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[1] This report is from a dissertation submitted by Sarah Ratner in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

[2] Birch and Harris, *Biochem. J.*, **24**, 1080 (1930).

[3] Shinohara, *J. Biol. Chem.*, **110**, 263 (1935).

[4] Schubert, *ibid.*, **111**, 671 (1935); **114**, 341 (1936).

[5] In this, 20 to 30%, according to the conditions, of the equivalent amount of nitrogen is set free, but this anomaly may be ascribed, as in the case of cystine [Laugh and Lewis, *ibid.*, **104**, 601 (1934)], to oxidative side reactions; under suitable conditions as much as 10% of the sulfur is converted into sulfuric acid by the reaction of nitrous acid.

[6] Du Vigneaud and Meyer, *ibid.*, **98**, 295 (1932); **99**, 143 (1932).

[7] Formaldehyde does not influence the titration curve at this point.

ing the change in rotation. Six buffered reaction mixtures between pH 1.5 and pH 12 were investigated at 25°. The velocity curves (Fig. 2) display a measurable rate of reaction which increases rapidly on raising the pH, and above 5 becomes too fast to follow.

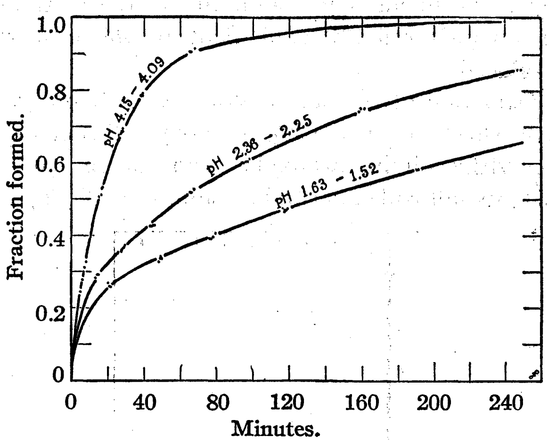

Fig. 1.—Rate of thiazolidinecarboxylic acid formation.

Thiazolidinecarboxylic acid behaves as an ampholyte (Fig. 3); the acidic dissociation (pK_1 1.51) is strong, but the basic dissociation (pK_2 6.21) extremely weak in comparison with those of α-amino acids in general, including proline (Table I).

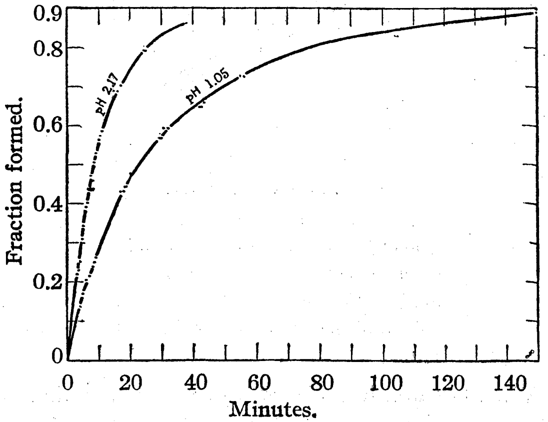

Fig. 2.—Rate of reaction of acetylcysteine and formaldehyde.

Replacement of the labile hydrogen atoms in thiazolidinecarboxylic acid produces changes in dissociation constants which are similar in direction to those which accompany similar substitutions in other amino acids.[8] The constants for the methyl ester and the acetyl derivative demonstrate the weakening effect, on both acidic and basic dissociation, of the inhibition of the ionizing function of one group (Figs. 5 and 6).

TABLE I

DISSOCIATION CONSTANTS OF AMINO ACIDS, THIAZOLIDINECARBOXYLIC ACID AND RELATED COMPOUNDS

	pK_1	pK_2
Alanine[a]	2.61	9.72
Cysteine[b]	1.96	8.18
S-Ethylcysteine	2.03	8.60
Proline[c]	1.99	10.60
Thiazolidine-4-carboxylic acid	1.51	6.21
Acetylthiazolidine-4-carboxylic acid	2.96	..
Methyl thiazolidine-4-carboxylate	..	4.00
Thiazolidine	..	6.31

[a] Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923). [b] Cannan and Knight, *Biochem. J.*, **21**, 1384 (1927). [c] McCay and Schmidt, *J. Gen. Physiol.*, **9**, 336 (1926).

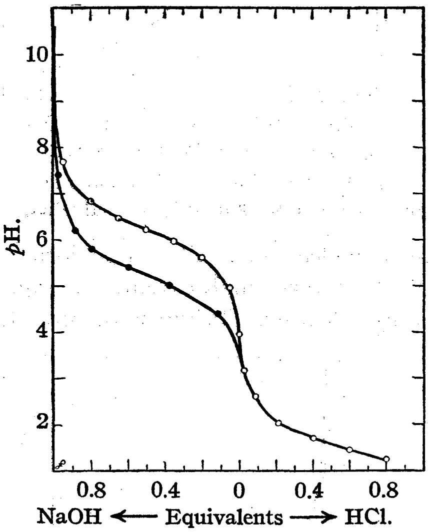

Fig. 3.—Titration of thiazolidinecarboxylic acid ○–○ in water and ●–● in 18% formaldehyde.

In the presence of a large amount of formaldehyde, the basic dissociation of thiazolidinecarboxylic acid is decreased (Fig. 3) but to a smaller extent than in proline and in S-ethylcysteine (Fig. 4). The presence of the $-CH_2S-$ group in the thiazolidine ring presumably exerts approximately the same effect on the basic dissociation constant as the introduction of a single hydroxymethyl group into a primary amino acid. The effect of formaldehyde upon the basic dissociation of thiazolidinecarboxylic acid, namely, depression by about one pK unit, is probably much the same as that of the second hydroxymethyl group in a compound of two molecules of formaldehyde with one of a primary amino acid.[9]

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(8) Cohn, *Ergebnisse Physiol.*, **33**, 781 (1931).

(9) Levy, *J. Biol. Chem.*, **79**, 767 (1933).

Acetylation or esterification of thiazolidinecarboxylic acid has no tendency to open the ring, and the corresponding derivatives are obtained in excellent yields.

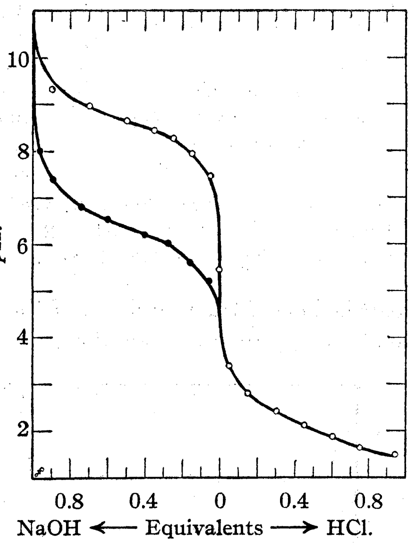

Fig. 4.—Titration of S-ethylcysteine ○–○ in water and ●–● in 18% formaldehyde.

Hydrolytic cleavage in *N* hydrochloric acid occurs only to a very small extent, and can be detected only when equilibrium is disturbed, as by removal of formaldehyde. A solution of thiazolidinecarboxylic acid in *N* hydrochloric acid was heated in a sealed tube at 100° for twenty-four hours; the rotation remained essentially unchanged. On the other hand, hydrolysis was detected by distilling the solution at constant volume. Formaldehyde was found in the distillate in amounts roughly equivalent to the cysteine produced.

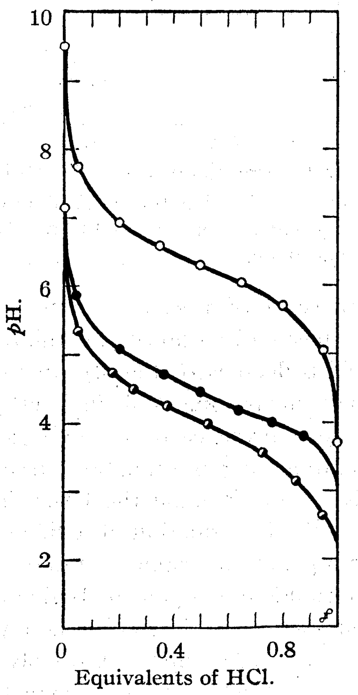

Fig. 5.—Titration of thiazolidine ○–○ in water, ●–● in 18% formaldehyde and ◐–◐ in methyl thiazolidinecarboxylate.

Oxidation of the sulfur atom exerts a progressive effect in increasing carboxyl dissociation. Acetylthiazolidinecarboxylic acid has a *pK* of 2.96, its sulfoxide 2.50 and its sulfone 2.23 (Fig. 6).

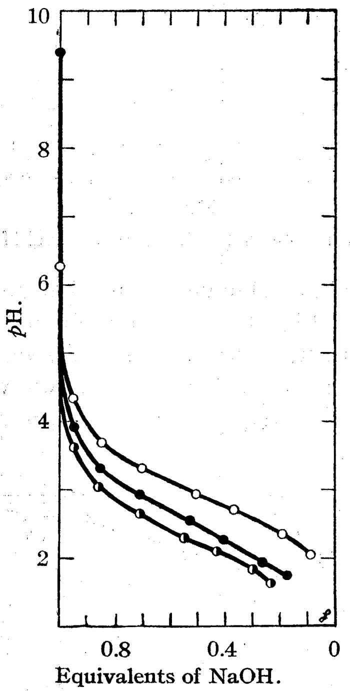

Fig. 6.—Titration of ○–○ acetylthiazolidinecarboxylic acid, ●–● acetylthiazolidinecarboxylic acid sulfoxide and ◐–◐ acetylthiazolidinecarboxylic acid sulfone.

With hot alkaline plumbite in an atmosphere of nitrogen, lead sulfide is formed from thiazolidinecarboxylic acid, but more slowly than from cysteine.[10] The first evidence of its formation was noticed after twenty-five minutes at 95°; after twenty-four hours 97.5% of the theoretical amount had precipitated.

With iodoacetic acid and benzyl chloride, which react with sulfhydryl groups,[11] the corresponding

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(10) Fruton and Clarke, *J. Biol. Chem.*, **106**, 667 (1934); Blumenthal and Clarke, *ibid.*, **110**, 343 (1935).

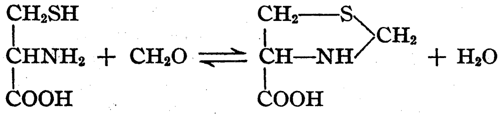
(11) Dickens, *Biochem. J.*, **27**, 1141 (1933); Michaelis and Schubert, *J. Biol. Chem.*, **106**, 331 (1934).

cysteine derivatives are formed from thiazolidinecarboxylic acid in alkaline solution (*p*H 10–11) at room temperature.

Ring opening may also be demonstrated at *p*H 10 by the action of air in the presence of a trace of ferric chloride; cystine is formed slowly. Other oxidizing agents bring about ring opening more readily: one equivalent of hydrogen peroxide or of iodine produces cystine and formaldehyde almost quantitatively. With bromine water, cysteic acid is formed, six equivalents of the halogen being consumed.

Thiazolidinecarboxylic acid reacts with sulfite apparently to form an equilibrium mixture. The progress of the reaction, which is rapid at *p*H 5 or above, can be measured at *p*H 4 by following the change in optical rotation. Sulfhydryl is formed in the process, for an increasing power to reduce phosphotungstic acid is observed. Thiazolidinecarboxylic acid alone does not reduce phosphotungstic acid at *p*H levels below 11.

All these observations may be interpreted as indicating the existence of an equilibrium



which lies so far to the right that sulfhydryl reactions are ordinarily imperceptible. Disturbance of this equilibrium by an irreversible process displaces it to the left.

Acetylation changes this behavior considerably. Iodine does not oxidize acetylthiazolidinecarboxylic acid, and hydrogen peroxide in suitable organic solvents yields the corresponding sulfoxide and sulfone, which are stable in aqueous solution. The sulfoxide is reduced by hydrogen iodide, with liberation of two equivalents of iodine; the sulfone is not affected in this way.

The parent thiazolidine, prepared for purposes of comparison by the condensation of β-aminoethyl mercaptan with formaldehyde, is a stable liquid of weakly basic character (Fig. 5 and Table I), and displays chemical properties analogous to those of the carboxylic acid. Its basic dissociation is depressed by formaldehyde (Fig. 5) to a greater extent than is the case with the carboxylic acid. With acetic anhydride it yields an acetyl derivative which is not oxidized by iodine but on treatment with two moles of hydrogen peroxide in glacial acetic acid yields a crystalline sulfone; the corresponding sulfoxide could not be obtained in crystalline form. The free base is oxidized by iodine to di-β-aminoethyl disulfide and by bromine to taurine. The boiling point, 164–165°, is notably higher than that of thiazole (117°); that of thiazoline (138–139°) occupies an intermediate position.

Experimental

Thiazolidine-4-carboxylic Acid.—The cysteine hydrochloride from 30 g. of cystine was dissolved in 100 cc. of water; 22 cc. of commercial 40% formaldehyde (1.1 mole) was added, and the mixture allowed to stand overnight at room temperature. On the addition of 25 cc. of pyridine, crystals soon separated. The whole was diluted with 50 cc. of alcohol and filtered. The product (28.2 g.) was recrystallized from hot water. The resulting long, colorless needles, which melt with decomposition at 196–197°, are insoluble in alcohol, somewhat soluble in cold water, readily soluble in hot water, in acid and in alkali.

Anal. Calcd. for $C_4H_7O_2NS$: C, 36.06; H, 5.26; N, 10.52; S, 24.05. Found: C, 35.93; H, 5.27; N,[12] 10.38; S, 24.09. $[\alpha]^{20}_D$ −141° in water; $[\alpha]^{22}_D$ −100° in *N* hydrochloric acid; $[\alpha]^{22}_D$ −203° in *N* sodium hydroxide.

The specific rotation was also determined at a series of *p*H levels in suitable buffered solutions, the *p*H values of which were determined potentiometrically.

TABLE II

*p*H	1.52	2.25	4.09	6.10	9.88
$[\alpha]^{25}_D$	−120	−135	−142	−173	−214

A solution in 10–15% hydrochloric acid, when allowed to evaporate at room temperature *in vacuo*, deposited the hydrochloride as large quadrangular prisms, m. p. 184–185° with decomposition, readily soluble in alcohol.

Anal. Calcd. for $C_4H_7O_2NS{\cdot}HCl$: N, 8.26; Cl, 20.91. Found: N, 8.08; Cl, 21.00.

When a concentrated aqueous solution is diluted with water, the free acid crystallizes out.

Thiazolidinecarboxylic Acid Methyl Ester Hydrochloride.—A solution of 10 g. of thiazolidinecarboxylic acid in 100 cc. of methanol which had been saturated with dry hydrogen chloride was warmed under reflux on a steam-bath for one hour. The solution was evaporated to a small volume *in vacuo*, ether was added, and the crystalline product chilled, filtered off and dried *in vacuo* over solid alkali; yield 13 g. (94%). It was recrystallized by dissolving in methanol and precipitating with ether, and appears as shiny plates which decompose at 164–165°; very soluble in water and alcohol, insoluble in ether.

Anal. Calcd. for $C_5H_9O_2NS{\cdot}HCl$: Cl, 19.31; S, 17.46; N, 7.63; CH_3O, 16.89. Found: Cl, 19.39; S, 17.74; N, 7.60; CH_3O, 16.76.

Methyl Thiazolidinecarboxylate.—To a suspension of 13 g. of ester hydrochloride in 3–4 cc. of water, covered with about 30 cc. of ether, anhydrous potassium carbonate was added slowly in excess. The ether was decanted

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[12] As most of the compounds described in this paper gave low values for nitrogen by the micro-Dumas method, the micro-Kjeldahl process was employed throughout. Grateful acknowledgment is made to Mr. William Saschek for the analytical results here reported.

after shaking. Extraction with ether was repeated several times. The combined ethereal solution was dried with barium oxide and the ether removed; the residual crude oil was distilled *in vacuo;* b. p. 75° (1.0 mm.); yield 7.85 g. (75%).

Anal. Calcd. for $C_5H_9O_2NS$: CH_3O, 21.08; S, 21.79; mol. wt., 147. Found: CH_3O, 21.14; S, 21.82; mol. wt., 149.2, 146.6 (cryoscopic in C_6H_6). $[\alpha]^{23}\mathrm{D}$ -83.0 in water; $[\alpha]^{21}\mathrm{D}$ -106.3 in benzene; $[\alpha]^{21}\mathrm{D}$ $-94.7°$ in CH_3OH; d^{23}_4 1.324; $n^{25}\mathrm{D}$ 1.527.

The ester showed no tendency to condense with itself even on long standing.

Acetylthiazolidinecarboxylic Acid.—To a suspension of 9.3 g. of thiazolidinecarboxylic acid in 30 cc. of water, 30 cc. of acetic anhydride was added slowly at 90° with constant stirring over a twenty-minute period. The clear solution was heated for forty minutes longer. Water and acetic acid were removed *in vacuo*, the residue dissolved in 30 cc. of hot water. On cooling, crystals appeared as six-sided prisms which were filtered off after chilling; yield 10.0 g. (82%), m. p. 143.5–144.5°; very soluble in water, somewhat less so in alcohol, acetone and ether.

Anal. Calcd. for $C_6H_9O_3NS$: C, 41.11; H, 5.18; N, 8.00. Found: C, 40.92; H, 5.07; N, 7.85. $[\alpha]^{20}\mathrm{D}$ -133.5 in water (*p*H 2.1); $[\alpha]^{20}\mathrm{D}$ $-159.8°$ in an equivalent quantity of dilute sodium hydroxide.

Acetylation of Sodium Salt of Thiazolidinecarboxylic Acid.—Into a 10-cc. volumetric flask was weighed 0.875 g. of thiazolidinecarboxylic acid (5 mml.); 5 cc. of *N* sodium hydroxide and 3.0 cc. of acetic anhydride (30 mml.) was added and the volume made up to 10 cc. with water. The flask was kept at 37° and 2-cc. samples were withdrawn after 46, 92 and 168 hours. To each sample 12.7 cc. of *N* sodium hydroxide was added, followed after three hours by 6.85 cc. of 2 *N* sulfuric acid. The solution was taken to dryness *in vacuo;* the residue was extracted with 20 cc. of hot absolute ethyl alcohol, the alcohol was evaporated and the residue so obtained recrystallized from a small amount of water. $[\alpha]^{23}\mathrm{D}$ $-133.2°$ after 46 hours; $-134.4°$ after ninety-two hours; $-134.4°$ after one hundred and sixty-eight hours.

Phenylalanine when treated in exactly the same way was found to be completely racemized after twenty-four hours.

Effect of *p*H on Velocity of Formation (Figs. 1, 2).—All solutions were made up so that 25 cc. contained 1.70 mml. each of cysteine hydrochloride (or acetylcysteine) and formaldehyde, 15 cc. of the appropriate 0.1 *N* buffer (or sodium chloride solution of equivalent ionic strength) with appropriate amounts of acid or alkali. The initial rotation for each curve was determined by omitting formaldehyde from the solution, and the final values were determined from equimolar solutions of thiazolidinecarboxylic acid. The final value of the cysteine reaction mixture agreed with the rotation calculated for the end-product. The *p*H of all solutions were determined with the glass electrode. Despite buffering, a change in *p*H (about 0.1) occurs during the reaction owing to the large difference between the *pK*'s of cysteine and thiazolidinecarboxylic acid. The initial and final *p*H values are recorded on the curves. The concentrations of the acetylcysteine and cysteine hydrochloride stock solutions were calculated from Kjeldahl nitrogen determinations and the formaldehyde stock solution was analyzed by iodine titration.

The values plotted in the curves were those of X calculated from the formula

$$\alpha_0\,(1 - X) + \alpha_\infty X = \alpha_{\text{obsd.}}$$

In the experiments with acetylcysteine, the value for α_∞ was based upon the final steady value observed in the reaction mixture.

Titration Curves (Figs. 3–6).—Except in the formaldehyde titrations, 0.1 *M* solutions were titrated with *N* sodium hydroxide and hydrochloric acid. The *p*H measurements, made with a glass electrode,[13] are reliable to ±0.03. The values reported (pK_1 for the acid constants and $pK_2 = pK_b - pK_w$ for the basic constants) each represent the average of the values calculated from five points in the curve. In the formaldehyde titrations, 5 cc. quantities of 0.1 *M* solution were added to 100 cc. of 18% formaldehyde and titrated with 0.1 *N* sodium hydroxide. All curves were corrected for water blanks.

Hydrolysis of Thiazolidinecarboxylic Acid.—A solution of 0.3021 g. of the acid in 25 cc. of *N* hydrochloric acid was distilled slowly for nine hours with addition of water at the approximate rate of distillation. The distillate, which amounted to 100 cc., was collected under alcoholic dimedon solution; it yielded 65 mg. of the formaldehyde derivative, m. p. 187°.

The residual solution was made up to 25 cc.; it gave a strong reaction with nitroprusside. The observed rotation (2 dcm. tube) of the solution before distillation was $-2.47°$; after distillation $-2.04°$. The fall in rotation corresponds to a conversion of 15.3% of the thiazolidinecarboxylic acid into cysteine having[14] $[\alpha]\mathrm{D}$ $+7.6°$.[15] The cysteine content, determined by the Lugg modification[16] of the method of Folin and Marenzi, was 11.0%.

Reaction with Iodoacetic Acid.—A solution of 0.66 g. of thiazolidinecarboxylic acid (5 mml.), 0.93 g. of iodoacetic acid (5 mml.) and 1.04 g. of potassium carbonate (15 m. eq.) in 10 cc. of water was allowed to stand overnight at room temperature. Upon the addition of 10 cc. of *N* hydrochloric acid crystals slowly appeared. The yield of S-carboxymethyl cysteine[11] was 0.77 g. (87%); thin trapezoidal plates from water, m. p. 200° (dec.).

Anal. Calcd. for $C_5H_9O_4NS$: H, 5.06; C, 33.51; N, 7.82. Found: H, 4.88; C, 33.33; N, 7.87 (Van Slyke amino N).

Reaction with Benzyl Chloride.—A mixture of 0.66 g. of thiazolidinecarboxylic acid, 0.63 g. of benzyl chloride and 0.69 g. of potassium carbonate in 10 cc. of water was stirred for twenty-four hours at room temperature. S-Benzylcysteine crystallized out during the reaction; m. p. 210° (dec.), unchanged by admixture with an authentic sample;[17] $[\alpha]\mathrm{D}$ $+23.8°$ in *N* sodium hydroxide.

Action of Oxygen in Alkaline Solution.—A solution containing 0.266 g. of thiazolidinecarboxylic acid (2 mml.), 2 cc. of *N* sodium hydroxide, 5 cc. of half-neutralized 0.2 *M*

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(13) A modification by F. Rosebury of the apparatus described by him in *Ind. Eng. Chem., Anal. Ed.*, **4**, 398 (1932).

(14) Assuming $[\alpha]\mathrm{D}$ $+15.9°$ [Vickery and Leavenworth, *J. Biol. Chem.*, **86**, 129 (1930)] the conversion would be 14.3%.

(15) Toennies and Bennet, *J. Biol. Chem.*, **112**, 499 (1936).

(16) Lugg, *Biochem. J.*, **26**, 2160 (1932).

(17) Clarke and Inouye, *J. Biol. Chem.*, **94**, 549 (1932).

bicarbonate buffer and 0.1 cc. of 0.01 *M* ferric chloride was made up to a volume of 10 cc. Air was passed through the solution for twenty-four hours at room temperature. The *p*H (10.2) was then brought to 6.4 by the addition of 2 cc. of *N* hydrochloric acid. After several days hexagonal plates had separated. The product, weighing 8 mg. (3.3%), was identified as cystine.

Oxidation with Hydrogen Peroxide.—A solution of 0.266 g. of thiazolidinecarboxylic acid in 30 cc. of water and 0.12 cc. (1.05 equiv.) of 30% hydrogen peroxide was allowed to stand at room temperature for several days; regular hexagonal plates separated; yield 0.210 g. (87%) of cystine; $[\alpha]_D$ $-214.5°$ in *N* hydrochloric acid. The filtrate was distilled into alcoholic dimedon; 0.408 g. (70%) of the formaldehyde derivative was secured.

Oxidation with Iodine.—To 10 cc. of 0.1 molar thiazolidinecarboxylic acid was added 10 cc. of 0.1 *N* iodine in 2.5% potassium iodide. The iodine was decolorized rapidly and regular hexagonal plates soon separated. Pyridine (0.2 cc.) was added and after two days 0.100 g. (83%) of cystine was obtained; $[\alpha]^{22}_D$ $-212°$ in *N* hydrochloric acid.

The filtrate yielded 0.141 g. (50%) of the dimedon derivative of formaldehyde, m. p. 187°.

On titration with iodine, 1.6–1.7 equivalents were consumed by thiazolidinecarboxylic acid, 1.0–1.2 by its methyl ester. The consumption of iodine in excess of one equivalent is attributable to oxidation of cystine.[18]

Oxidation with Bromine.—A solution of 0.2896 g. (2.175 mml.) of thiazolidinecarboxylic acid in 10 cc. of water was titrated at 0° with *N* bromine in acetic acid. The end-point, taken when the yellow color persisted for thirty seconds, was reached with 6.45 mml. of bromine (5.94 equivalents). The resulting solution was evaporated to dryness *in vacuo*, and the crystalline residue purified by repeated precipitation from water by absolute alcohol. $[\alpha]^{24}_D$ $+7.7°$ in water. The cysteic acid was identified as the copper salt.

Anal. Calcd. for $C_3H_7O_6NSCu$: N, 5.63; S, 12.89; Cu, 25.56. Found: N, 5.57; S, 13.22; Cu, 25.77.

Action of Sulfite on Thiazolidinecarboxylic Acid.—To a solution of 1.5 mml. was added 15 mml. of sodium sulfite, suitably buffered and the volume made up to 25 cc. The optical rotation of the resulting solution was determined at intervals:

OBSERVED ROTATIONS (2 DCM.) AFTER SPECIFIED TIMES

*p*H	0	5 min.	15 min.	20 min.	30 min.	95 min.	8 hrs.
4.03	−2.26°	−2.02°		−1.80°		−1.66°	−1.66°
6.41	−2.80°		−0.96°		−0.92°		

The zero values, determined in the absence of sulfite, were obtained by interpolation from the *p*H dependence data (Table II).

Action of Phosphotungstic Acid and Sulfite on Thiazolidinecarboxylic Acid.—To 2 cc. of 0.00832 molar thiazolidinecarboxylic acid was added 2 cc. of phosphotungstic acid solution, buffered to *p*H 5.7, according to the directions of Lugg.[16] No appreciable color appeared. When 1 cc. of molar sodium sulfite was incorporated in an otherwise similar mixture, a blue color appeared; this continued to increase in intensity at a rate considerably less than that observed with cystine. Comparison with cystine standards showed after thirteen hours a color intensity equivalent to 43% of that observed with an equimolar quantity of cystine.

In another experiment, 50 cc. of 0.00832 molar thiazolidinecarboxylic acid was mixed with 20 cc. of molar sulfite, and diluted to 100 cc. The color developed with phosphotungstic acid was determined at intervals under the conditions described by Lugg. The color intensities, expressed as percentages of that of the equimolar cystine standard, were

Hours	0.1	4	10	22
Color	11	27	28	28

With twice the amount of sulfite, the maximum color developed after six hours was 47%; after ninety-three hours, it had fallen to 30%. No attempt was made further to investigate the effect of variations in the proportion of sulfite.

Sulfoxide of Acetylthiazolidinecarboxylic Acid.—A solution of 0.876 g. (5 mml.) of acetylthiazolidinecarboxylic acid in 40 cc. of acetone was treated with 0.6 cc. (5.25 mml.) of 30% hydrogen peroxide. After three days the solvent was evaporated under reduced pressure. The residue was recrystallized by adding acetone to its solution in the minimum quantity of hot alcohol: 0.690 g. of octagonal prisms, m. p. 188–190° (dec.); $[\alpha]^{26}_D$ $-118°$ in water.

Anal. Calcd. for $C_6H_9O_4NS$: C, 37.67; H, 4.75; N, 7.33; neut. eq., 191. Found: C, 37.57; H, 4.90; N, 7.32; neut. eq., 190.

The same product was obtained in substantially the same yield by the use of twice the above proportion of hydrogen peroxide in acetone.

A weighed amount (30.6 mg.) of the sulfoxide was added to a solution containing 1 cc. of 5 *N* KI and 0.5 cc. of 10 *N* HCl. After an hour 3 cc. of water was added and the solution quantitatively transferred to a separatory funnel with 5 cc. more water. The iodine extracted with peroxide-free ether and titrated with 0.1 *N* thiosulfate, required 3.23 cc. (2.02 equivalents).

Sulfone of Acetylthiazolidinecarboxylic Acid.—To a solution of 0.876 g. (5 mml.) of acetylthiazolidinecarboxylic acid in 20 cc. of glacial acetic acid (distilled over chromic anhydride) 1.5 cc. (11 mml.) of 30% hydrogen peroxide was added. After seven days the acetic acid was removed *in vacuo*. The crystalline residue (0.77 g.) was twice recrystallized from 10 cc. of hot alcohol; trilateral prisms, m. p. 190° (dec.); $[\alpha]^{25}_D$ $-90.8°$ in water.

Anal. Calcd. for $C_6H_9O_5NS$: C, 34.76; H, 4.38; N, 6.76; neut. eq., 207. Found: C, 35.10; H, 4.48; N, 6.70; neut. eq., 205.

The compound liberated practically no iodine from acidified potassium iodide solution.

Thiazolidine.—Twelve grams of phthalimidoethyl mercaptan[19] was hydrolyzed by boiling for twelve hours under reflux with a mixture of 120 cc. of 20% hydrochloric acid

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(18) Simonsen, *J. Biol. Chem.*, **101**, 35 (1933); Shinohara, *ibid.*, **96**, 285 (1932).

(19) Gabriel, *Ber.*, **24**, 1110 (1891).

and 20 cc. of glacial acetic acid. After cooling, phthalic acid was filtered off, and the filtrate was concentrated *in vacuo*, filtered again, and finally taken to dryness in a vacuum desiccator over potassium hydroxide. The crude aminoethyl mercaptan hydrochloride[20] was dissolved in 20 cc. of water, treated with 4.6 cc. of formalin, allowed to stand overnight, and taken to dryness *in vacuo*. The residue was crystallized from alcohol; yield, 6.63 g. (91%) of long needles; m. p. 180° (dec.).

Anal. Calcd. for $C_3H_7NS{\cdot}HCl$: C, 28.66; H, 6.42; S, 25.53; N, 11.15; Cl, 28.24. Found: C, 28.86; H, 6.76; S, 25.77; N, 10.88; Cl, 28.1.

The free base, liberated from the above hydrochloride by potassium carbonate, is readily volatile with steam, miscible in all proportions with water, and can be salted out readily with potassium carbonate. It is a colorless liquid, b. p. 164–165°, d^{25}_4 1.131, n^{30}_D 1.551.

Anal. Calcd. for C_3H_7NS: N, 15.72; C, 40.39; H, 7.92. Found: N, 15.77; C, 40.40; H, 7.80.

Acetylthiazolidine.—An excess (2.5 cc.) of acetic anhydride was added to 1.51 g. of the free base; the acetic acid was removed *in vacuo*, and the residual liquid distilled under reduced pressure; b. p. 83–85° (0.7 mm.); yield 1.96 g. (88%).

Anal. Calcd. for C_5H_9ONS: C, 45.76; H, 6.91; N, 10.68. Found: C, 44.66; H, 6.74; N, 10.24.

Sulfone of Acetylthiazolidine.—To a solution of 0.712 g. of acetylthiazolidine in 10 cc. of glacial acetic acid, 1.5 cc. (2.3 mole) of hydrogen peroxide was added. After a week the solvent was removed *in vacuo* and the residue recrystallized from hot alcohol; stout hexagonal prisms or long plates, m. p. 122°.

Anal. Calcd. for $C_5H_9O_3NS$: C, 36.78; H, 5.56; N, 8.58. Found: C, 36.72; H, 5.33; N, 8.65.

Oxidation of Thiazolidine with Bromine.—*N* Bromine in acetic acid was added to 0.354 g. (4 mml.) of thiazolidine in 5 cc. of water to a faint permanent yellow (5.8 equivalents). The solution was taken to dryness *in vacuo*, and the residue recrystallized by adding alcohol to a concentrated solution in water. The product, taurine, formed fine needles, was neutral in reaction and did not melt below 260°; yield, 0.430 g. (86%).

Anal. Calcd. for $C_2H_7O_3NS$: N, 11.19. Found: N, 10.95.

Oxidation of Thiazolidine with Iodine.—To 0.3358 g. of free thiazolidine (3.77 mml.) in 5 cc. of water was added 37.7 cc. of 0.1 *N* iodine in 2.5% potassium iodide. A white solid appeared which redissolved slowly. After twenty hours the colorless solution was filtered to remove a small red precipitate, and 3.77 cc. of *N* sodium hydroxide was added. A colorless solid which precipitated was filtered off. Formaldehyde was identified in the filtrate. The colorless precipitate, apparently an aldehyde–ammonia, was dissolved in excess hydrochloric acid, when a strong odor of formaldehyde was evolved. The solution was taken to dryness *in vacuo* and the residue recrystallized from ethyl alcohol. The resulting needles, 0.250 g., m. p. 206°, were identified as di-β-aminoethyl disulfide hydrochloride, described by Gabriel.[21]

Anal. Calcd. for $C_4H_{12}N_2S_2{\cdot}2HCl$: N, 12.43. Found: N, 12.33.

Summary

Formaldehyde reacts with cysteine over a wide range of *p*H to form thiazolidine-4-carboxylic acid, the mode of formation, constitution and properties of which are here discussed.

Thiazolidine, similarly prepared from formaldehyde and β-aminoethyl mercaptan, is also described.

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[20] Gabriel, *Ber.*, **22**, 1137 (1889).

[21] Coblenz and Gabriel, *ibid.*, **24**, 1122 (1891).

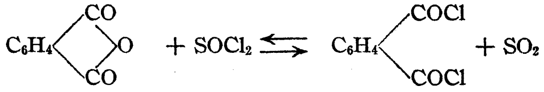
NEW YORK, N. Y. RECEIVED OCTOBER 31, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MONSANTO CHEMICAL CO.]

Phthalyl Chloride

BY L. P. KYRIDES

Phthalyl chloride has been prepared by the interaction of phthalic anhydride and phosphorus pentachloride.[1] Thionyl chloride converts phthalic acid into the anhydride, but is reported to have no action on the latter at refluxing temperatures even in presence of catalysts or pyridine.[2] We found that excellent yields of phthalyl chloride are readily obtained if the reaction is carried out at elevated temperatures in presence of very small amounts of anhydrous zinc chloride.[3] We also observed that the reaction is reversible, since thionyl chloride is obtained when sulfur dioxide and phthalyl chloride react at around 200°, also in presence of zinc chloride. The reaction is, therefore, expressed as



$$C_6H_4\left\langle\begin{matrix}CO\\ \ \ \ \ \ \ \rangle O\\ CO\end{matrix}\right. + SOCl_2 \rightleftarrows C_6H_4\left\langle\begin{matrix}COCl\\ \\ COCl\end{matrix}\right. + SO_2$$

If no zinc chloride is present and thionyl chloride

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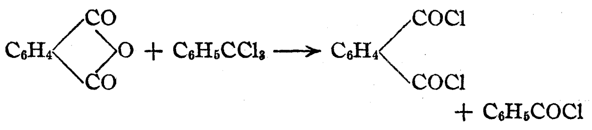
[1] Bruehl, *Ann.*, **235**, 13 (1886).

[2] Meyer, *Monatsh.*, **22**, 437 (1901); McMaster and Ahmann, THIS JOURNAL, **50**, 145 (1928); Carré and Libermann, *Compt. rend.*, **199**, 1422 (1934).

[3] U. S. Patent 1,951,364.

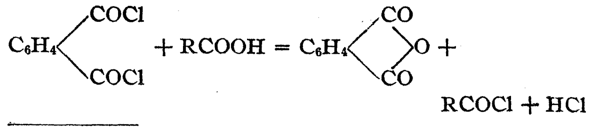
is dropped very slowly into phthalic anhydride at 220° over a period of forty hours, only about 70% of the anhydride is converted into phthalyl chloride. Meyer[2] had observed that thionyl chloride converts maleic and succinic acids into anhydrides but not into chlorides. Fumaryl and succinyl chlorides are obtained in good yields if the reaction is carried out in presence of zinc chloride.

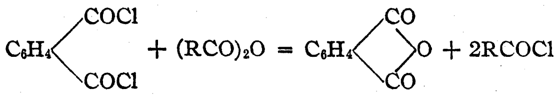
Benzotrichloride has been used in a limited number of cases for the preparation of chlorides from monocarboxylic acids and their anhydrides. Phthalic anhydride and benzotrichloride did not react at 200°; but the addition of a trace of zinc chloride induced a distinct reaction. By increasing the amount of zinc chloride, the conversion proceeded at a fairly rapid rate even as low as 100°.[4] The reaction products were separated easily by simple fractionation. This reaction takes place as follows



The phthalyl chloride obtained by all of the processes contains small amounts of dissolved anhydride, an observation which had also been made by Bruehl[1] in the phosphorus pentachloride reaction. The solubility of the anhydride in phthalyl chloride is of the order of 5–6% at 15°, so that it is easy to free it from an excessive amount of anhydride by filtration after cooling. The phthalyl chloride containing dissolved anhydride is perfectly satisfactory for most reactions.

Van Dorp and Van Dorp[5] found that phthalyl chloride and fumaric acid reacted at 120–160° to give a good yield of fumaryl chloride. We have used phthalyl chloride in many reactions and found it to be an excellent reagent for the nearly quantitative conversion of acids and anhydrides into acid chlorides. If the boiling points of these chlorides are not too close to those of phthalyl chloride and phthalic anhydride, they can be obtained in very pure form by direct fractionation. The reactions take place as follows





Maleic and succinic anhydrides are converted into chlorides with phthalyl chloride only in presence of zinc chloride as is the case with thionyl chloride.

Experimental

1. Phthalyl Chloride from Phthalic Anhydride and Thionyl Chloride.—The apparatus consisted of a three-necked flask, with an efficient reflux condenser, a dropping funnel and an agitator (the latter being used only in case large amounts of materials were to be made).

Three hundred grams of phthalic anhydride and 1.5 g. of technical anhydrous zinc chloride were charged into the flask and the mixture was heated over a wire gauze to 220°. The theoretical amount of thionyl chloride (241 g.) was dropped in over a period of about ten hours, at such a rate that the temperature could be maintained at about 220°. The reaction mass was distilled directly under a vacuum of 4.5 mm. and 380 g. of a liquid distillate was obtained boiling at 119–122°. After standing cold for some time, a small amount of phthalic anhydride separated out, which after isolation weighed 22 g. The filtered phthalyl chloride analyzed 94% by chlorine analysis, so that the conversion amounted to 86% and the yield was practically quantitative on the anhydride consumed.

2. Thionyl Chloride from Phthalyl Chloride and Sulfur Dioxide.—A mixture of 107 g. of phthalyl chloride (94%) and 2 g. of zinc chloride was heated at 200°. A slow current of sulfur dioxide was bubbled through the mixture and the distillate was condensed using running water. After a ten-hour reaction, 44.3 g. of a distillate had collected which upon redistillation gave 39 g. of thionyl chloride, which amounts to 66% of the theoretical yield from phthalyl chloride. No attempt was made to analyze the unreacted sulfur dioxide for its thionyl chloride content. Since, however, the residue from the reaction was practically chlorine free, it is presumed that a considerable portion of the thionyl chloride was lost with the uncondensed gas.

3. Phthalyl Chloride from Phthalic Anhydride and Benzotrichloride.—A mixture of 225 g. of phthalic anhydride, 290 g. of fractionated benzotrichloride (sp. gr. 1.38) and 20 g. of zinc chloride was heated in an oil-bath at 110–120° overnight (reaction time twenty hours) and the reaction mixture was fractionated carefully under a vacuum of about 23 mm. The fractions consisted of 201 g. of benzoyl chloride boiling at 90–95°; 8.8 g. boiling up to 138° and 287 g. of phthalyl chloride boiling mostly at 150–152°.

The phthalyl chloride fraction upon standing cold deposited a few crystals of phthalic anhydride, indicating that it was about 95% pure. The theoretically expected weight yields of phthalyl and benzoyl chlorides were 308 and 208 g., respectively.

The residue from the distillation containing the zinc chloride was found capable of promoting the reaction of fresh quantities of reactants. It was also found that zinc oxide and zinc dust can be used as catalysts in place of zinc chloride. The activity of these is, no doubt, due to their transformation to zinc chloride in the reaction mixture.

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(4) U. S. Patent 1,963,748; 1,963,749.

(5) Van Dorp and Van Dorp, *Rec. trav. chim.*, **25**, 96 (1906).

If the amount of zinc chloride is reduced to one-tenth of that used in this experiment, the temperature has to be raised to about 200° in order that the reaction may proceed at a fairly rapid rate.

When *o*-chlorobenzotrichloride was used in place of benzotrichloride, the reaction products consisted, as was to be expected, of phthalyl and *o*-chlorobenzoyl chlorides.

4. **Butyryl Chloride from Phthalyl Chloride.**—A flask connected to a short fractionating column was charged with 340 g. of phthalyl chloride, heated at about 140° and treated slowly with 132 g. of *n*-butyric acid. Hydrogen chloride was evolved as the acid was added and part of the butyryl chloride distilled over. Finally, vacuum was applied and the remainder of the chloride recovered. Refractionation gave 146.5 g. of butyryl chloride which represents a 91.5% yield of the theoretical on butyric acid.

5. **Fumaryl Chloride from Maleic Anhydride.**—A mixture of 98 g. of maleic anhydride, 231 g. of 94% phthalyl chloride and about 0.5 g. of zinc chloride was heated overnight at about 140°. Vacuum was applied and the fumaryl chloride distilled until phthalic anhydride began to separate in the condenser. The distillate, amounting to 146 g., was found to contain 129 g. of fumaryl chloride and 15 g. of unreacted maleic anhydride. The yield, therefore, of the chloride on the anhydride which was consumed was nearly quantitative.

The writer is indebted to Messrs. M. N. Dvornikoff and O. J. Weinkauff for assistance in the experimental part of the investigation.

Summary

Phthalyl chloride can be made in good yields from thionyl chloride or benzotrichloride and phthalic anhydride at elevated temperatures using zinc chloride as catalyst and, reversibly, thionyl chloride is formed from the interaction of sulfur dioxide with phthalyl chloride under the same conditions.

Acid chlorides can be produced in excellent yields from the interaction of acids or their anhydrides with phthalyl chloride.

In the case of the anhydrides of acids, such as succinic and maleic acids, which do not react directly with phthalyl or thionyl chlorides, the reaction can be catalyzed with traces of zinc chloride to give good yields of the desired acid chlorides.

ST. LOUIS, MO. RECEIVED NOVEMBER 5, 1936

[CONTRIBUTION NO. 45 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Mellitic Acid from Coals, Cokes and Graphites

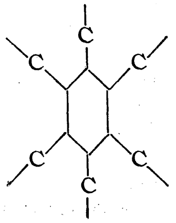
BY BERNARD JUETTNER

Carbonization of coal involves the loss of volatile decomposition products such as gas, tar and water, and the formation of a condensed, non-volatile residue. The more important factors influencing the degree of condensation of the residue are: the final temperature, the rate of heating and the nature of the coal. Another factor may be the speed at which the decomposition products are removed, which in turn depends largely on the thermal variables mentioned above, on the pressure in the retort during the carbonization, and on the particle size of the coal.[1,2] The ash of the coal may also exert an influence due to catalytic effects.

The purpose of this work is to determine the degree of condensation of various carbonaceous materials, by conversion of these high molecular weight condensed bodies into small identifiable units of structural significance. The development of such a method permits the evaluation of the relative importance of such variables as maximum temperature, heating rate and specific nature of the material.

To accomplish the purpose in view the oxidation reagent employed must be powerful enough to penetrate to the last skeletal nuclei, but should not result in complete breakdown to carbon dioxide.

Mellitic acid, the benzene hexacarboxylic acid, is known as an oxidation product of various carbonaceous materials. It forms a relatively insoluble ammonium salt and hence can be determined nearly quantitatively; it is very resistant to further oxidation, and is of definite structural significance, since it can only be formed from such structures as



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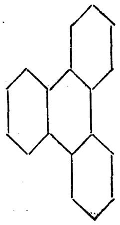

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[1] Lowry, *Ind. Eng. Chem.*, **26**, 321 (1934).

[2] Juettner and Howard, Coal Research Lab., Carnegie Inst. of Tech., Contrib. No. 8; Juettner and Howard, *Ind. Eng. Chem.*, **26**, 1115 (1934).

or more condensed bodies. It therefore appeared that a systematic study of the yields of this acid obtained from various condensed carbonaceous materials would contribute to the end in view.

There is wide disagreement in the literature as to the yield of mellitic acid obtainable by oxidation of carbonaceous materials. This is no doubt due to variation in the nature of the materials themselves, the oxidation reagent employed and to the technique used in isolating the acid. In many cases no mention of yields is made.[3] In the recent work of Meyer and Raudnitz,[4] carbons from various sources were oxidized by refluxing with nitric acid (sp. gr. 1.5–1.52) and 0.2% vanadic acid for eighty hours. If the solution was still dark after twenty hours, sulfuric acid was added and boiling continued. The crude mellitic acid was converted into the ammonium salt. This had to be purified through the copper salt. Their yields, which are the highest in the literature, are based on the crude ammonium salt. The yield of pure mellitic acid is not given.

The few references[5] in the literature to yields of mellitic acid obtained by the oxidation of coals and cokes report values of 1% or less, or do not make any quantitative statements. Nearly the same quantity, 0.6% of mellitic acid, was found in this Laboratory[6] by oxidizing Edenborn coal for thirty days with 1 *N* nitric acid. Even after two months of refluxing with the dilute nitric acid the oxidation was very incomplete, not reaching the skeletal nuclei. Therefore a search was made for a reagent that would attack the condensed structure and yet not destroy the mellitic acid formed. Under such conditions the maximum yield of this acid should be obtained. Mellitic acid is reported not to be oxidized by boiling concentrated nitric acid nor by alkaline permanganate. It therefore appeared that in this respect these reagents would meet our requirements.

Experimental

Characteristics of Coal, Cokes and Graphites.—In this work only one coal and the various cokes prepared from it were oxidized. This coal, a Pittsburgh seam coal from the Edenborn Mine, is described in detail in a Bureau of Mines publication.[7] The 500° coke was prepared in a rotating Fischer retort at a heating rate of 1.9° per minute. The temperature was held at 500° for one hour. All the other cokes were prepared in a small tube retort at varying heating rates.[8] The final temperature was maintained for one hour. The artificial graphite was an Acheson graphite electric furnace electrode. All these materials were ground to pass 200 mesh. Only the natural graphite was of smaller particle size. This graphite is known as "Dixon Micronized" No. 200–05.

Oxidation Procedures.—Since it was desirable that the oxidation method be applicable to a wide range of coals, cokes and other carbons, the 500° Edenborn coke was selected as a product of intermediate complexity suitable for evaluation of the various processes.

Alkaline Permanganate Oxidation.—Samples of 100 g. were oxidized with an excess of permanganate in three liters of water containing 200 g. of potassium hydroxide for one week. The oxidation was carried out in an iron vessel provided with water cooled lid and stirrer. Any excess permanganate still present at the end of the experiment was destroyed with formic acid. The manganese dioxide was filtered off and washed thoroughly.

The filtrate was concentrated and the following methods were used in an attempt to recover the free acids. (1) The concentrated filtrate was acidified with sulfuric acid and the salts recovered on evaporation were extracted with ether and acetone. This procedure was used by Bone.[9] The recovery was very poor. (2) The filtrate was acidified with hydrochloric acid and the solution poured into a large excess of methyl alcohol. The precipitate, potassium chloride, was filtered off and the filtrate evaporated to dryness. Again the recovery was incomplete and the acids high in inorganic residue. (3) The concentrated filtrate was placed in the middle cell of a three-compartment dialyzer with a parchment membrane on the acid and cellophane on the alkaline side. After electrolysis for four days with a current of 3–4 amp. the acids were found to have migrated completely to the anode compartment. Cathodic and anodic compartments were emptied and refilled with distilled water twice during twenty-four hours. No organic material was found in the cathode liquors, but in cases of incomplete oxidation the larger molecular weight compounds remained in the middle compartment. The combined anodic solutions were evaporated to dryness and the non-volatile acids weighed. The ash content of the free acids was usually less than 0.5% and never more than 1.0%.

The acids were dissolved in 300 cc. of warm water and poured into 1.5 liters of concentrated ammonium hydroxide. The ammonium hydroxide precipitate consisted, in the case of the alkaline permanganate oxidations, mainly of hydrated ammonium oxalate, which is only moderately soluble under these conditions. To obtain the free acids the ammonium hydroxide precipitate was electrolyzed.

The acids recovered by evaporation of the anodic solution to dryness were esterified with diazomethane. The

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(3) For a review see Treibs, *Ges. Abhandl. Kenntnis Kohle*, **5**, 580–587 (1920). Meyer and Jacobson, "Lehrbuch der organ. Chemie," Vol. II, pt. 1, p. 592.

(4) Meyer and Raudnitz, *Ber.*, **63B**, 2010–2018 (1930).

(5) Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle*, **5**, 200 (1920); Fischer, Schrader and Treibs, *ibid.*, **5**, 235, 319 (1920–21). Fuchs and Stengel, *ibid.*, **9**, 130 (1926–29); Bone and Quarendon, *Proc. Roy. Soc.* (London), **A110**, 537 (1926); Bone, Horton and Ward, *ibid.*, **A127**, 480 (1930); Bone, Parsons, Sapiro and Groocock, *ibid.*, **A148**, 492 (1935).

(6) Juettner, Smith and Howard, THIS JOURNAL, **57**, 2322 (1935).

(7) Bur. Mines Tech. Paper 525 (1932).

(8) Warren, *Ind. Eng. Chem.*, **27**, 72, 1350 (1935).

(9) Bone, Horton and Ward, *Proc. Roy. Soc.* (London), **A127**, 489 (1930).

esters were placed in a molecular fractionating still. When the heating bath temperature was 100° dimethyl oxalate distilled over (0.001 mm.). The residue in the still was purified by recrystallization from methyl alcohol and water and found to be the hexamethyl ester of mellitic acid. *Anal.* Calcd.: C, 50.71; H, 4.23. Found: C, 50.81; H, 4.21. M. p. of authentic sample 187°; mixed m. p. 186°.

The dimethyl oxalate was recrystallized from chilled ether. *Anal.* Calcd.: C, 40.66; H, 5.12. Found: C, 40.77; H, 5.12.

The ammonium oxalate was also determined by titration with 0.1 *N* permanganate in sulfuric acid solution, mellitic acid not being oxidized under these conditions.

Oxidation with Nitric Acid (Sp. Gr. 1.5).—One hundred grams of the 500° coke was refluxed for fourteen days with 1500 cc. of fuming nitric acid to which 0.24 g. of ammonium vanadate was added. The whole mixture was then evaporated to dryness on a steam-bath under vacuum. The solid residue was weighed, dissolved in water, made alkaline and electrolyzed in the usual manner. Ammonium mellitate was precipitated as before. The use of nitric acid alone resulted in the formation of a large amount of complex oxidation products which on electrolysis remained in the center compartment, even in the presence of excess alkali.

Nitric Acid Followed by Alkaline Permanganate (Standard Procedure).—After drying and weighing, the residue from the nitric acid treatment was further oxidized with an excess of alkaline permanganate for seven days, and the excess permanganate destroyed with formic acid. The manganese dioxide was filtered off and washed thoroughly. The filtrate was concentrated and electrolyzed. The acids from the anode compartment were recovered by evaporation. After first drying and weighing the acids were redissolved in 300 cc. of warm water, filtered and poured into 1500 cc. of ammonium hydroxide (sp. gr. 0.9). The mixture was chilled to 0° under constant stirring and held there for one-half hour. This procedure has been used throughout our work and was found much more satisfactory than saturation with ammonia gas from the standpoint of reproducibility and pure precipitation. However, it should be kept in mind that 4 g. of mellitic acid remains in solution under these conditions and is lost. By using nitric acid first and then alkaline permanganate the highest yields of mellitic acid were obtained. The ammonium hydroxide precipitate was found to be pure ammonium mellitate, shown to be free from oxalic acid by failure to reduce 0.1 *N* permanganate in acid solution. This procedure was later adopted as standard.

Nitric Acid Followed by Acid Permanganate and then by Alkaline Permanganate.—After refluxing in the same manner with nitric acid, the acid was diluted with an equal volume of water and a solution of 50 g. of potassium permanganate was run into the boiling acid. The whole was then evaporated to dryness in vacuum on the water-bath. When all nitric acid had been eliminated, the residue was treated with excess potassium hydroxide solution and further oxidized with permanganate. The acid permanganate appears to oxidize the mellitic acid to some extent under these conditions.

Examination of Ammonium Precipitates from the Various Procedures.—The ammonium precipitate from the procedure using alkaline permanganate alone consisted mainly of ammonium oxalate monohydrate. The corresponding precipitates from the three other procedures did not consume any 0.1 *N* permanganate when titrated for oxalic acid. All these precipitates were white. The weight was taken after drying for forty-eight hours over sulfuric acid under reduced pressure. Under these conditions the precipitate had the approximate composition of a hexahydrate. *Anal.* Calcd.: C, 26.09; H, 6.52; N, 15.22. Found: C, 26.22; H, 6.20; N, 15.80; ash, 0.05. Ammonium mellitate is reported[10] to form a nonahydrate, $C_6(COONH_4)_6 \cdot 9H_2O$.

A suitable mixture for electrolysis was found to be 10 g. of ammonium precipitate, 14 g. of potassium hydroxide, and about 4 cc. of 85% formic acid. In one experiment, for example, 136.6 g. of ammonium mellitate was dissolved in 2000 cc. of water containing 200 g. of potassium hydroxide and 55 cc. of formic acid. The whole was split in two equal portions and electrolyzed in two dialyzers. The current was not allowed to exceed 4 amp. at 110 volts. The evaporation residue from the anodes was dried for eighteen hours on the steam-bath and then for four days in high vacuum over phosphoric anhydride at room temperature. The weight of the residue after that time was 86.82 g. There was still a slight weight change after four days' drying. Recoveries on smaller samples from individual oxidations were of the same order.

Anal. Calcd. for $C_{12}H_6O_{12}$: C, 42.10; H, 1.75. Found: C, 41.94; H, 1.95; ash, 0.17.

Identification by Means of the Neutral Methyl Ester.—The acid recovered by electrolysis was esterified with diazomethane. Recrystallization from methyl alcohol, to which hot water was added, yielded, on cooling, the colorless needles of the hexamethyl ester: m. p. 187°, giving no depression when mixed with an authentic sample of the ester. Determinations of the yield of ester were made on individual specimens and also on a composite sample representing the greater number of the experiments. The yield of the pure ester averaged 84% of the theoretical.

Amounts of Reagents Used.—In all cases a large excess of reagents was used: 1500 cc. of nitric acid, sp. gr. 1.50, was used per 100 g. An excess of potassium permanganate was also used. For the original coal the amount was about 2.0 g. of permanganate per g., in a week's oxidation; for the cokes the quantity used decreased with increasing carbonization temperature, about 3.5, 1.5 and 1.0 g. per gram of coke being used for the 500, 700 and 1000° cokes, respectively, in a one-week oxidation period; for the graphites about 9.0 g. per gram was used in a two-week period.

Carbon Balance.—In all cases the carbon was oxidized to carbon dioxide, mellitic acid, and acids soluble in ammonium hydroxide. Tests showed that 4 g. of mellitic acid remained dissolved in ammonium hydroxide under our conditions. By evaporating the residual liquid in the center compartment of the dialyzer only silica was found.

To determine whether any organic material was lost when the manganese dioxide was filtered off, it was dissolved in hydrochloric acid and filtered. With the cokes small amounts of silica were found, but no organic matter.

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[10] Beilstein's "Handbuch der organ. Chemie."

With the artificial graphite, 9.0 g. of apparently unchanged graphite was obtained; with the natural graphite 7.6 g. No trace of graphitic acid or any other intermediate oxidation product was found.

Discussion

Effects of Reagents on Yields of Mellitic Acid.—Table I shows the yield of mellitic acid by the alkaline permanganate oxidation to be small and of little significance. From Table II it is evident that the oxidation procedure which gives the highest yield of mellitic acid from the 500° coke is nitric acid followed by alkaline permanganate, and that the yield is adversely affected by the use of the acid permanganate intermediate stage. This effect is much more marked in the case of the 1000° coke: when nitric acid and alkaline permanganate were used 22.5 g. of mellitic acid was recovered per 100 g. By the additional use of acid permanganate only 10.3 g. of mellitic acid was obtained. Nitric acid followed by alkaline permanganate was therefore chosen as the standard procedure.

TABLE I

OXIDATION OF COAL AND COKE WITH ALKALINE PERMANGANATE

Per 100 g.	Edenborn coal	500° Edenborn coke	500° Edenborn coke
C per 100 g.	78.27	80.17	80.17
Time of oxidation, hours	7	7	280
Non-volatile acids after electrolysis, g.	85.0	97	67.3
Oxalic acid, g. (calcd. from ammonium oxalate)	30	22	12.4
Mellitic acid, g. (calcd.)[a]	1.02	2.92	3.37
Hexamethyl ester of mellitic acid obtained, g.	0.61	0.81	1.78

[a] Calculated from yield of ammonium mellitate using an experimentally determined conversion factor of 0.636.

TABLE II

ACTION OF OTHER OXIDIZING AGENTS ON 500° EDENBORN COKE

100 g. coke	Mellitic acid recovered, g.
Alkaline permanganate for 280 hours	3.37[a]
Nitric acid	7.25
Nitric acid + alkaline permanganate	11.9
Nitric acid + acid permanganate + alkaline permanganate	10.9

[a] Calculated from ammonium mellitate.

Reproducibility and Losses of Standard Procedure.—In Table III the results of three parallel experiments with the 500° coke are given and show good agreement. The losses occurring, when mellitic acid was subjected to the standard procedure, are shown in the same table and probably can largely be attributed to manipulative losses rather than to oxidation of the mellitic acid itself.

TABLE III

REPRODUCIBILITY AND LOSSES IN STANDARD PROCEDURE

	Residue after nitric acid treatment, g.	Acids after alk. permanganate oxidation, g.	Mellitic acid recovered, g.
100 g. 500° Edenborn coke	95.5	29.7	11.9
	96.2	30.8	11.5
	96.3	28.8	11.5
100 g. mellitic acid	97.5	87.5	83.5

Effect of Carbonization Temperature on the Yield of Mellitic Acid.—From the data given in Table IV it is evident that condensation progresses rapidly up to 700°, where an apparent stability is reached. It should be emphasized that only up to a certain stage should the yield of mellitic acid be expected to increase as condensation takes place and that beyond this point a decrease would be expected, since in large C_6 ring structures a greater fraction of the carbon would necessarily appear as carbon dioxide. When it is taken into account that 4 g. of mellitic acid remained in the ammonium hydroxide during precipitation the ratio of the yields of mellitic acid from coal and coke is greatly increased over that calculated from the data in the table. To assist in the interpretation of the results on coal and coke, oxidations were also carried out, by the standardized procedure, on a natural and on an artificial graphite, where presumably a high degree of condensation is reached.

TABLE IV

EFFECT OF TEMPERATURE OF CARBONIZATION ON YIELD OF MELLITIC ACID

Edenborn 100 g.	Coal	500° Coke	540° Coke	700° Coke	1000° Coke
Heating rate, °C./min.	...	1.9	1.4	1.4	1.4
Carbon per 100 g.	78.27	80.17	79.47	79.80	86.74
Residue after nitric acid oxidation, g.	70.1	95.5	100.6	79.4	50.9
Acids after permanganate oxidation, g.	28.1	29.7	29.1	39.7	29.4
Mellitic acid recovered, g.	5.5	11.9	15.5	24.1	22.5

Oxidation of Artificial and Natural Graphites.—The standard procedure was applied, except that the oxidation period with alkaline permanganate was increased to two weeks. At the end of that time the permanganate was still being decolorized slowly. The material recovered after the nitric acid oxidation resembled ordinary graphite, in both cases, but when treated with alkaline permanganate the oxidizing agent was consumed at a rapid rate. In the case of the Acheson graphite the permanganate was reduced at a rate of about 9 g. per hour at first; after two weeks the rate fell to 1.7 g. per hour. A parallel experiment was made with the Acheson graphite not pre-oxidized with nitric acid. In this case the alkaline permanganate oxidation was very slow, the rate of reduction being 1–2 g. per hour at first and remaining constant for one week, when the experiment was discontinued. To study the effect of particle size, "Aquadag," a colloidal graphite, was also oxidized and unexpectedly gave a smaller yield of mellitic acid than the other graphites.

The data in Table V show that carbonic and mellitic acids are the principal oxidation products of natural and artificial graphite. From these figures we see that in the oxidation of a highly condensed cyclic substance, such as graphite, only a small portion of the carbon is utilized for mellitic acid formation; by far the largest part is converted to carbon dioxide, since large condensed structures have to be destroyed to get to the mellitic acid nucleus. This suggests that the structure which would give the optimum yield of mellitic acid would be one containing many small aromatic "islands," such "islands" being the results of a small crystal size in the case of certain graphites, or the interposition in the lattice of such atoms as oxygen, nitrogen or sulfur in the case of cokes. From a continuous cyclic system, such as graphite is generally believed to be, we had expected only carbon dioxide. For a better interpretation of highly condensed carbons by means of mellitic acid yields much more work is needed, especially the effect of the nature of the original carbon during carbonization and also the effect of particle size in the oxidation should be studied. Further work to that end is in progress.

TABLE V

OXIDATION OF GRAPHITES

100 g. samples	Acheson electrode graphite, −200 mesh	Natural graphite "Micronized Dixon Graphite"	"Aquadag" per 100 g. dry materia
Carbon per 100 g.	99.5	97.4	..
Residue after nitric acid oxidation, g.	71.0	78.5	21.5
Acids after permanganate oxidation, g.	23.7	26.9	14.5
Mellitic acid recovered, g.	19.1	21.7	8.3

Effect of Heating Rate on the Yield of Mellitic Acid from Cokes.—Cokes prepared at a maximum temperature of 540° but heated at a rate of 1.4°/minute and 21.8°/minute, and at maximum temperatures of 700 and 1000° with heating rates of 1.4, 5.5 and 21.8°/minute, respectively, were oxidized using the standard procedure. The yields of mellitic acid showed only slight variations for the cokes prepared at a given temperature, from which it follows that the final temperature of carbonization is the most important factor in determining the yields of mellitic acid obtained.

It should be mentioned that these yields of mellitic acid are the highest for any pure organic compound other than carbonic and oxalic acids obtained from coal or coke. The yields given in the tables are those actually recovered. Since it was shown that 4 g. is lost in the ammonia precipitation, the mellitic acid formed would be greater by this amount over the yields shown in the tables.

Acknowledgments.—The author wishes to thank H. C. Howard, F. C. Silbert and W. B. Warren of this Laboratory for assistance and cooperation in this work.

Summary

Alkaline permanganate, nitric acid, nitric acid followed by alkaline permanganate and nitric acid followed successively by acid permanganate and alkaline permanganate have been used in the oxidation of coal, cokes and graphites to mellitic acid. The action of nitric acid followed by alkaline permanganate is particularly effective in oxidizing a wide range of carbonaceous materials to mellitic acid. Neither reagent alone is satisfactory. With alkaline permanganate alone little mellitic acid is formed and large amounts of oxalic acid. With nitric acid alone mellitic acid is recovered and no oxalic acid, but the yield of mellitic acid is low due to the formation of intermediate oxidation products of high molecular weight. By subsequent alkaline permanganate treatment these intermediates are oxidized to mellitic acid. This is well illustrated by the behavior of graphite. Nitric acid or permanganate alone have no visible effect on graphite, but by oxidation with nitric acid first, followed by alkaline permanganate, 19.1 g. of mellitic acid was recovered per 100 g. of artificial graphite. This yield is of the same order as that from a natural

graphite and from the 700 and 1000° Edenborn cokes.

The effect of the carbonization temperature of the coke on the yield of mellitic acid was studied. From Edenborn coal, little mellitic acid was obtained. With increasing carbonization temperature the yield increased rapidly up to 700°. With the 1000° coke about the same quantity was recovered as with the 700° coke. With high temperature cokes the interpretation of our results becomes difficult. There is at present no satisfactory explanation for the uniformity of mellitic acid yields from such widely different carbons as 700 and 1000° cokes, artificial and natural graphites.

Cokes with the same final carbonization temperatures but widely different heating rates show small differences in the mellitic acid yield, which probably does not have important significance.

Pittsburgh, Penna. Received October 12, 1936

[Contribution from the Department of Chemistry, University of Notre Dame]

Some Ethers of 3-Butyn-1-ol[1]

By P. A. McCusker and J. W. Kroeger

In view of the commercial availability of certain derivatives of ethylene glycol commonly known as Cellosolves and Carbitols, it was proposed to investigate the preparation and properties of acetylenic compounds derived from these starting materials. This group of compounds, the 1-alkoxy-3-butynes, provides not only a new type of acetylene for investigation but also furnishes a starting point for further syntheses since the terminal hydrogen of the chain is quite labile, being attached to a triply bonded carbon atom.

Various types of acetylenic ethers are reported in the literature[2] the majority of which are ethers of propargyl alcohol. Of the group of compounds described herein, all are new with the exception of 1-methoxy-3-butyne which was prepared by Lespieau[3] by dehydrohalogenation.

The technique of the preparation of acetylenic compounds as originally described by Picon,[4] who treated sodium acetylide in liquid ammonia with alkyl iodides, has been modified in this Laboratory to apply to alkyl bromides. The Cellosolves and Carbitols were converted to the corresponding bromides by the method of Palomaa and Kenetti.[5] Of these, 2,2′-dibromodiethyl ether and ethyl 2-bromoethyl glycol ether, the bromides derived from diethylene glycol and diethylene glycol monoethyl ether, respectively, are new compounds. The acetylenes were obtained from these various bromides in yields of 60 to 75% according to the type reaction

$$\mathrm{R{-}O{-}CH_2{-}CH_2Br + NaC{\equiv}CH \longrightarrow R{-}O{-}CH_2{-}CH_2{-}C{\equiv}CH + NaBr}$$

These acetylenes are quite stable to light and air. Carefully purified samples were water-white after standing for three months. The characteristic odor of the 1-alkynes is unusually powerful in these acetylenic ethers.

Sodium acetylide does not react appreciably with 2,2′-dichlorodiethyl ether, under the experimental conditions used. Ethylene bromohydrin when treated with sodium acetylide is converted to acetaldehyde, principally.

Experimental

Preparation of Bromides.—Commercial samples of the various glycol derivatives were treated with phosphorus tribromide in the presence of pyridine.[4] Redistillation of the glycol ethers was usually unnecessary. The physical constants for 2,2′-dibromodiethyl ether, which has not previously been reported, are: b. p. 115° (32 mm.); $n^{27}\mathrm{D}$ 1.5131; $d^{27}{}_4$ 1.8222. The constants for ethyl, 2-bromoethyl glycol ether are: b. p. 100–101° (33 mm.); $n^{24}\mathrm{D}$ 1.4580; $d^{24}{}_4$ 1.3340.

Preparation of Acetylenes.—One liter of liquid ammonia was placed in a 3-liter three-necked flask and stirred vigorously while a rapid stream of acetylene was bubbled through. To this, 1.2 moles (excess) of sodium dissolved in liquid ammonia was added slowly. When all the sodium had been converted to sodium acetylide, one mole of bromide was slowly dropped in and the mixture was stirred for two to four hours. Five hundred milliliters of water was then added and the organic layer which separated was washed with dilute hydrochloric acid, then with saturated

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[1] Eighteenth paper on the chemistry of the alkyl acetylenes and their addition products; previous paper, This Journal, **58**, 1861 (1936).

[2] Lespieau, *Compt. rend.*, **194**, 287 (1932); Yvon, *ibid.*, **180**, 748 (1925); Grard, *Ann. chim.*, **13**, 336 (1930); Liebermann, *Ann.*, **135**, 266 (1865).

[3] Lespieau, *Compt. rend.*, **144**, 116 (1907).

[4] Picon, *ibid.*, **158**, 1346 (1914); **169**, 32 (1919).

[5] Palomaa and Kenetti, *Ber.*, **64B**, 797 (1931); Tallmann, This Journal, **56**, 127 (1934).

TABLE I

PROPERTIES OF COMPOUNDS R—O—C_2H_4—C≡CH

R—	B. p., °C.	Mm.	n_D	Temp., °C.	d_4	MR_D Calcd.	MR_D Found	Hg deriv., m. p., °C.
CH—^{3}	87.5	748	1.4117	22	0.8505	24.9	24.6	113.9
C_2H_5—	104.0	747	1.4148	22	.8273	29.6	29.7	98.6–99.0
C_4H_9—	147–148	747	1.4191	27	.8185	38.8	39.1	42.2–42.5
HC≡C—C_2H_4—CH_2—	164–165	750	1.4519	26	.8980	36.8	36.6	[a]
$BrCH_2$—CH_2—	99–100	35	1.4788	25	1.3271	37.3	37.8	85.0–86.0
C_2H_5—O—C_2H_4	84.5–85.5	34	1.4381	24	0.9267	40.23	40.25	[a]

[a] The mercury derivatives of these two compounds could not be crystallized and decomposed above 100°.

TABLE II

ANALYTICAL DATA

Compound	Calculated	Found
$C_2H_5OC_2H_4C≡CH$	C, 73.5; H, 10.2	73.3; 10.1
$C_4H_9OC_2H_4C≡CH$	C, 76.1; H, 11.2	75.8; 10.1
$C_2H_5OC_2H_4OC_2H_4C≡CH$	C, 67.5; H, 9.9	67.2; 9.3
$HC≡CC_2H_4OC_2H_4C≡CH$	C, 78.7; H, 8.2	78.4; 8.0
$BrC_2H_4OC_2H_4C≡CH$	Br, 45.1	45.3
$BrC_2H_4OC_2H_4Br$	Br, 68.9	68.7
$BrC_2H_4OC_2H_4OC_2H_5$	Br, 40.6	40.6
$(CH_3OC_2H_4C≡C)_2Hg$	Hg, 54.4	54.0
$(C_2H_5OC_2H_4C≡C)_2Hg$	Hg, 50.8	50.5
$(C_4H_9OC_2H_4C≡C)_2Hg$	Hg, 44.6	44.6
$(BrC_2H_4OC_2H_4C≡C)_2Hg$	Hg, 36.3	41.1[a]

[a] This derivative was apparently contaminated with a more highly mercurated compound.

sodium carbonate solution and finally was dried over sodium sulfate and fractionated. The properties of the acetylenes prepared in this manner are given in Table I. In the reaction of sodium acetylide with dibromodiethyl ether, some 2′-bromo-1-ethoxy-3-butyne was also obtained.

The mercury derivatives mentioned in Table I were prepared by the method of Johnson and McEwen[6] and were recrystallized from benzene.

Summary

1. Some new acetylenic ethers have been described.

2. The physical constants of 2,2′-dibromodiethyl ether and ethyl 2-bromoethyl glycol ether are reported.

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[6] Johnson and McEwen, THIS JOURNAL, **48**, 471 (1926).

NOTRE DAME, IND.

RECEIVED OCTOBER 22, 1936

NOTES

Concerning the Alleged Absorption of Gaseous Nitrogen by Benzene Solutions of Rubber and Guttapercha Hydrocarbons

BY LOUIS B. HOWARD[1] AND GUIDO E. HILBERT

Experiments described by De Jong[2] have been interpreted as indicating that dilute benzene solutions of rubber or guttapercha hydrocarbon from sheet balata, when exposed to sunlight for a few days in either quartz or ordinary glass vessels, absorb gaseous nitrogen in appreciable amounts.[3] If such a photochemical combination of rubber and nitrogen actually occurs, one might reasonably expect other unsaturated hydrocarbons containing isoprene units such as carotene and xanthophyll to behave similarly. These substances which always are found closely associated with chlorophyll in green plants possess physiological functions which, as yet, remain quite obscure. It therefore seemed of very great importance from both a theoretical and a practical standpoint to attempt to confirm these results of De Jong.

In the present study the experimental procedure of the original investigation was followed as closely as the description of the work allowed. Several variable factors, such as temperature, barometric pressure, vapor pressure of the benzene solutions and the heating effect of sealing the tubes, were controlled. In one experiment Pyrex tubes of 150-cc. capacity were filled with

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[1] Now employed at the Whittier, Calif., station of the Bureau of Entomology and Plant Quarantine.

[2] De Jong, *Rec. trav. chim.*, **51**, 153 (1931).

[3] In one case a tube containing 54 cc. of a 1.05% solution of rubber in benzene under an atmosphere of nitrogen was found to draw in 11 cc. of water when opened under the surface of this liquid after six days of irradiation. This was considered to indicate an absorption of 12.8 mg. of nitrogen which according to his calculations represented 2.5% of the weight of the rubber.

100 cc. of nitrogen gas and 50 cc. of benzene solutions containing about 0.5% of either pale crepe rubber or balata. After sealing, these tubes and a benzene control were exposed to direct sunlight during the summer for various lengths of time up to five weeks. At the end of the tests the changes in volume of the nitrogen in the tubes containing the rubber solutions differed from that of the benzene control by a maximum of 0.5 cc. which was found to be about the limit of experimental error.

Another series of experiments was carried out in an apparatus which consisted of several volumetric reaction chambers in the form of glass tubes fitted with stopcocks and attached to a mercury leveling bulb. The tubes were charged with about 100 cc. of nitrogen and one, reserved for a control, with 50 cc. of pure benzene and the others with 50 cc. each of 1.1% benzene solutions of one of the following types of rubber: pale crepe (from a shipment just received), fine Para from South America, smoked sheet or balata. Even though the tubes were exposed to direct sunlight for three months during the summer the slight changes in volume of the gas were in every case less than 1 cc. and, in each of the rubber solutions, were actual *increases*.

It may be concluded that under the conditions described and with the specimens of rubber, nitrogen and benzene used, nitrogen gas is not absorbed to any appreciable extent.

Contribution from
Bureau of Chemistry and Soils
U. S. Department of Agriculture
Washington, D. C.
Received November 30, 1936

The Formation of Atacamite by the Incorporation of Copper Powder in Magnesium Oxychloride Compositions

By Dean S. Hubbell[1]

When magnesium oxychloride compositions that contain copper harden in the presence of air, the formation of a new phase is indicated by the development of a blue-green color as well as by an increase in strength and a reduction in solubility.

The new blue-green phase was found by X-ray examinations to be identical with atacamite and also cupric oxychloride prepared by dissolving freshly precipitated cupric carbonate in a solution of cupric chloride. This is in harmony with the observations of other investigators[2] who have shown that copper is corroded by certain chloride solutions in the presence of air to form a basic chloride resembling atacamite.

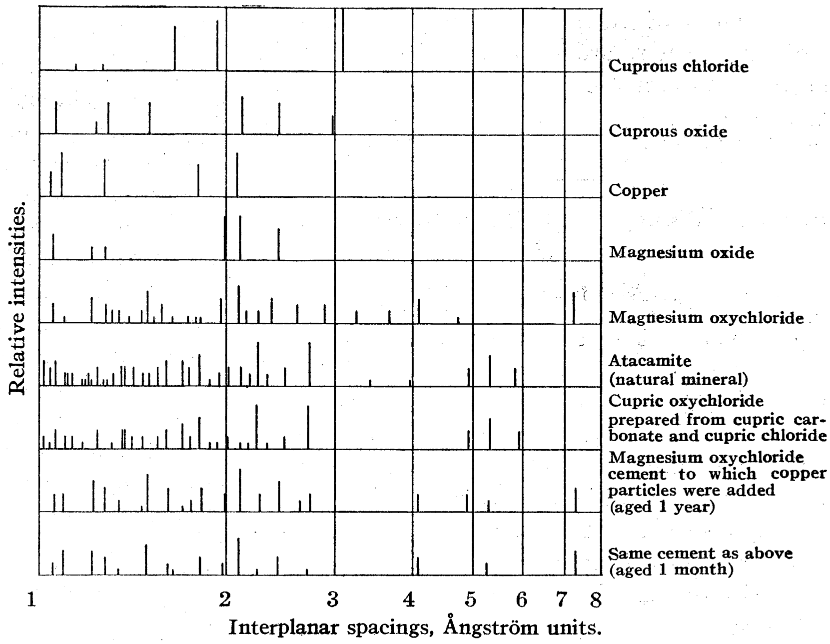

Fig. 1.—Diffraction data.

X-Ray diffraction analyses were made by the Debye–Scherrer method on a sample of the oxychloride cement after aging first for one month and then for one year. The radiation from an X-ray tube provided with a copper target was used, after filtering through nickel, in a camera of 57.3-mm. effective diameter. The specimens used were rods of 0.7-mm. diameter formed from the powdered samples with collodion as a binder. The interplanar spacings obtained from the photograms are shown in the accompanying figure, which includes data obtained in a similar way for cupric oxychloride, atacamite, magnesium oxychloride, copper, cupric chloride, cuprous chloride and magnesium oxide. The relative intensities of the corresponding diffraction lines were estimated visually.

Both unaged and aged oxychloride cements contain, as a major constituent, a material corresponding to magnesium oxychloride, as the similarity of the diffraction data indicates. Diffraction lines corresponding to the stronger

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[1] Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

[2] Benough and May, *J. Inst. Metals*, **32**, 131 (1924); Vernon and Whitby, *ibid.*, **34**, 389 (1930); Mellor, "Inorganic and Theoretical Chemistry," Vol. III, pp. 15, 69, 77, 150, 161; Rooksby and Churnside, *J. Soc. Chem. Ind., Trans.*, **53**, 33 (1934).

lines of cupric oxychloride, and of atacamite, but noticeably broad, were found for these cements, indicating that cupric oxychloride had been formed in appreciable amounts, but in very small, almost colloidal, particles. The amount of this compound is probably somewhat greater in the aged cement than in the unaged material. On the other hand, it is evident that cupric oxychloride has not formed a complex compound with magnesium oxychloride nor entered appreciably into solid solution in it.

It has been observed that the formation of the new phase takes place at the expense of the copper particles and that it cannot proceed in the absence of oxygen or of water vapor. Exposure to sunlight appears to retard and strong ultraviolet light prevents its formation.

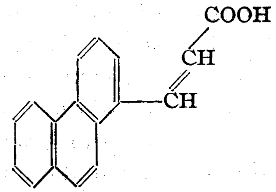
Mellon Institute
Pittsburgh, Penna.

Received November 2, 1936

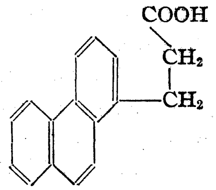
Rapid Synthesis of β-(1-Phenanthryl)-propionic Acid

By Samuel Natelson and Sidney P. Gottfried

1-Phenanthraldehyde, prepared by the method of Bachmann,[1] was converted rapidly in good yield to β-(1-phenanthryl)-propionic acid after the method described by the authors for a similar series.[2] 1-Phenanthraldehyde, which condenses with acetic anhydride and sodium acetate in extremely poor yield after the usual Perkin reaction, condenses almost quantitatively with malonic acid, with the elimination of carbon dioxide. The β-(1-phenanthryl)-acrylic acid formed (I) may be reduced to yield β-(1-phenanthryl)-propionic acid (II).[3] This acid has been prepared before by Bachmann[1] by a more tedious route in an attempt to synthesize 3′-keto-1,2-cyclopentenophenanthrene.



(I)



(II)

Ten grams of 1-phenanthraldehyde is mixed with 4 g. of malonic acid (excess) and 0.5 cc. of pyridine. The mixture is heated on a water-bath for thirty minutes, when effervescence ceases and the whole mass solidifies. The β-(1-phenanthryl)-acrylic acid, formed in almost quantitative yield, is washed with dilute acid to remove the pyridine and is recrystallized from acetone, m. p. 259°. This acid dissolved in dilute potassium hydroxide, is reduced with an excess of 3% sodium amalgam to yield 9–11 g. of β-(1-phenanthryl)-propionic acid (II), m. p. 187–188° (from acetone). It seems curious to the authors that reduction at the 9,10-positions of the phenanthrene nucleus was not brought about by the sodium amalgam.

Pediatric Research Laboratory
Jewish Hospital of Brooklyn
Brooklyn, N. Y.

Received November 16, 1936

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(1) Bachmann, This Journal, **57**, 1383 (1935); **58**, 2097 (1936).

(2) Natelson and Gottfried, *ibid.*, **58**, 1432 (1936).

(3) In a private communication, the authors have been informed by Bachmann that he corroborates these observations and has also successfully applied this series of reactions to several phenanthryl aldehydes.

COMMUNICATION TO THE EDITOR

SYNTHETIC VITAMIN B_1

Sir:

In our last communication [This Journal, **58,** 1504 (1936)] we reported synthetic vitamin B_1 chloride melting at 232–234° rather than at 246–250° as previously given for the natural product. We have, however, using our previous method but by a different choice of solvents for purification, obtained, in good yield, synthetic vitamin B_1 chloride which agrees in every particular with the natural vitamin. We owe thanks to Dr. G. A. Stein of the Merck Laboratories for his collaboration in this matter.

A low melting point has also been observed in the bromide. In both chloride and bromide the low melting point is associated with a much greater solubility in alcoholic solvents. Both low melting salts are obtained from methanol solutions by addition of ether. However, when recrystallized from methanol by addition of ethanol or from water by addition of ethanol, the higher melting forms have been obtained. The discrepancies in melting point and solubility are not paralleled by detectable discrepancies in composition, absorption spectra or physiological potency. Crystallographic and polarographic examinations have revealed a number of interesting features which, however, do not permit us to draw any final conclusions. The matter is still under investigation.

MERCK RESEARCH LABORATORIES
MERCK AND COMPANY, INC.
RAHWAY, NEW JERSEY
R. R. WILLIAMS
J. K. CLINE

RECEIVED NOVEMBER 23, 1936

NEW BOOKS

The Chemistry of the Colloidal State. A Textbook for an Introductory Course. Second edition. By JOHN C. WARE, Sc.M., Ph.D., Consulting Chemist. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1936. xvi + 334 pp. 96 figs. 15.5 × 23.5 cm. Price, $3.75.

This second edition, like the first, is clearly written in a style suitable for students who are not interested in a too mathematical discussion of colloid chemistry, and it should therefore find a place in colleges where such courses are taught.

The following additions have been made: A new chapter of six pages on Intermediate Cases—Soaps; one-half page on Edible Jellies; three paragraphs on emulsions; four pages on the precipitation of substances in the colloidal state; two paragraphs on the electrical character of interfacial phenomena; nine lines on the plating of rubber; nine lines on the Donnan equilibrium, and two pages on surface tension lowering. There is an over-all increase of twenty-one pages.

One is at a loss, however, to see how the author's statement that the text has been largely rewritten is justified. Many of the chapters are practically unchanged and there is no change in the figures. Also, the statement in the Preface that the space given to adsorption has been doubled actually finds little support, as twenty-eight pages are devoted to this topic in the first edition and twenty-nine in the second edition.

A. L. ELDER

Principles of Biochemistry. By ALBERT P. MATHEWS, Andrew Carnegie Professor of Biochemistry, University of Cincinnati. William Wood and Company, Mt. Royal and Guilford Avenues, Baltimore, Maryland, 1936. x + 512 pp. 15.5 × 24 cm. Price, $4.50.

A teacher for forty years who has "a profound respect and affection" for the "earnest, hard working and lively young people" who are his pupils should know their needs. And when he has in addition carried on continuous productive research in the field in which he teaches, he should be in a position to write a textbook which gives his students the information they need in a form at once interesting, critically accurate and up-to-date. This, we believe, Professor Mathews has accomplished in his new book.

The material is treated under the usual headings of Glucides, Lipides and Protides (the newer names for the familiar Carbohydrates, Fats and Proteins; then the Special Chemistry of Important Tissues, Vitamins and Hormones; and Energy Metabolism. In each case, the material selected is such as to give a clear and accurate picture to the student of both the chemistry and physiology of the material under discussion with relatively little of that rounding off of debatable topics which is necessary in the interest of clearness.

In the opinion of the reviewer, it is to be regretted that the author has, after due consideration, omitted almost all references to the literature because the student has not time to consult the original literature. This is conceded; also that only a small percentage of the students would do so if they had the time, since it is easier to accept authority than to try to get at the truth of the matter from published work. Nevertheless, the medical school is the last place where the student will get formal assistance in arriving at a critical view of what is going on in his field of interest, and, if he wishes to keep up with the advance of medicine during his lifetime, he should acquire the technique of critical reading before he leaves school. However, this is a minor point and detracts little, if at all, from the general excellence of the book.

W. R. BLOOR

Analytische Chemie der Edelmetalle. (Analytical Chemistry of the Noble Metals.) By Dr. ALFRED WOGRINZ, Lecturer at the Technical Institute of Vienna. Ferdinand Enke Verlag, Hasenbergsteige 3, Stuttgart W, Germany, 1936. xi + 141 pp. 14 figs. 16.5 × 25.5 cm. Price, RM. 13; bound, RM. 14.80.

The above book is essentially a compilation of the scattered information on the analytical chemistry of the noble metals. Fifty pages are devoted to silver, thirty to gold, and forty-five to the platinum metals. Under each of these headings the subject matter is presented similarly, being divided into a brief introduction of history and occurrence, followed by a discussion of analytical reactions, methods of detection and of determination, and procedures of separation, including those applicable to certain technical products. In addition, six pages are given over to tables of a number of physical properties. The book also contains an author and a subject index, and a list of works consulted. It is clearly printed on a good grade of paper.

The sections dealing with silver and gold appear to be quite complete, but that dealing with the platinum metals leaves the analytical chemistry of the group some twenty years out-of-date, owing to the fact, unfortunately, that consideration is not given to work done in recent years, the aim of which has been to replace the traditional methods of separation and of determination with others more in keeping with modern requirements of accurate chemical analysis. The section on the platinum metals, therefore, is more of historical interest than of practical value.

Raleigh Gilchrist

Annual Survey of American Chemistry. Volume X, 1935. Edited by Clarence J. West, Director, Research Information Service, National Research Council. Published by Reinhold Publishing Corporation, 330 West 42d Street, New York, N. Y., 1936. 487 pp. 14 × 22 cm. Price, $5.00.

It is advisable to list the topics reviewed in the latest volume of the annual Survey of American Chemistry because lack of space and the growing output of American chemists have made necessary the limitation of the fields covered in any one volume. The subjects included in Volume X are as follows: Theories of solution, the kinetics of homogeneous gas reactions, molecular structure, thermodynamics and thermochemistry, contact catalysis, inorganic chemistry, 1933–1935, analytical chemistry, 1934 and 1935, applications of X-rays in metallurgy, ferrous metallurgy, the platinum metals, electroörganic chemistry, aliphatic compounds, carbocyclic compounds, heterocyclic compounds, alkaloids, food chemistry, insecticides and fungicides, gaseous fuels, 1934 and 1935, petroleum chemistry and technology, detergents and detergency, cellulose and paper, synthetic plastics, rubber, unit processes in organic synthesis, chemical economics (1931–1935).

The amount of space given to any one research is necessarily small, but it is possible to find any details desired through the use of the complete list of references appended to each Chapter. It is of interest to note that the book contains over 4800 references—a fact that indicates the productivity of American chemists.

The high standard of the past has been maintained. The writer joins the editor in the belief that "the success of the series is due to the cordial and unselfish coöperation of the authors who have given so freely of their knowledge and experience." The editor also deserves praise for the excellence with which he has done his work.

James F. Norris

BOOKS RECEIVED

November 15, 1936–December 15, 1936

Konrad Bernhauer. "Gärungschemisches Praktikum." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 249 pp. RM. 12.60.

Karl K. Darrow. "The Renaissance of Physics." The Macmillan Company, 60 Fifth Ave., New York, N. Y. 306 pp. $3.00.

Th. de Donder and Pierre Van Rysselberghe. "Thermodynamic Theory of Affinity. A Book of Principles." Stanford University Press, Stanford Univ., Calif. 142 pp. $3.00.

Maurice Déribéré. "Les Applications Industrielle du *r*H. Le Potential d'Oxydo-Réduction." Dunod, Éditeur, 92 Rue Bonaparte, Paris, France. 98 pp.

F. G. Donnan and Arthur Haas. "A Commentary on the Scientific Writings of J. Willard Gibbs. Vol. I. Thermodynamics. Vol. II. Theoretical Physics." Yale University Press, New Haven, Conn. 742 + 645 pp. $10.00.

N. Feather. "An Introduction to Nuclear Physics." The Macmillan Company, 60 Fifth Ave., New York. 213 pp. $3.00.

R. H. Griffith. "The Mechanism of Contact Catalysis." Oxford University Press, 114 Fifth Ave., New York, N. Y. 208 pp. $5.00.

Joseph H. Keenan and Frederick G. Keyes. "Thermodynamic Properties of Steam, Including Data for the Liquid and Solid Phases." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 89 pp. + separate tables. $2.75.

Hubert Martin. "The Scientific Principles of Plant Protection with Special Reference to Chemical Control." Longmans, Green and Co., 114 Fifth Ave., New York, N. Y. 379 pp. $8.00.

Alwin Mittasch. "Über Katalyse und Katalysatoren." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 65 pp. RM. 3.60.

A. Sanfourche. "Le Contrôle Analytique dans l'Industrie Chimique Minérale." Masson et Cie., Éditeurs, 120 Boulevard Saint-Germain, Paris, France. 547 pp. Fr. 120.

H. A. Stuart and H. G. Trieschmann. "Lichtzerstreuung." Akademische Verlagsgesellschaft m. b. H., Sternwartenstrasse 8, Leipzig C, 1, Germany. 191 pp. RM. 24.

Robley Winfrey. "Statistical Analyses of Industrial Property Retirements." Bulletin 125, Iowa Engineering Experiment Station. Iowa State College of Agriculture and Mechanic Arts, Ames, Iowa. 176 pp.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 22, Kalium." Lieferung 1. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 246 pp. RM. 28.50.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 59, Eisen." Teil A, Lieferung 8. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 184 pp. RM. 24.37.

JOURNAL OF THE
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Seventh Report of the Committee on Atomic Weights of the International Union of Chemistry

BY G. P. BAXTER (*Chairman*), O. HÖNIGSCHMID AND P. LEBEAU

The following report of the Committee covers the twelve-month period, September 30, 1935, to September 30, 1936.[1]

The following changes in the table of atomic weights have been made:

Carbon, from 12.00 to 12.01
Rubidium, from 85.44 to 85.48
Gadolinium, from 157.3 to 156.9
Lead, from 207.22 to 207.21
Uranium, from 238.14 to 238.07

Oxygen.—Dole[2] reports a difference in isotopic composition between the oxygen of the air and that of the water of Lake Michigan, U. S., corresponding to 0.00008 atomic weight unit, and advocates some single isotope such as protium as atomic weight standard. Since analytical accuracy under the most favorable conditions does not surpass 0.001% and since the determination of atomic weights by chemical methods, no matter what standard is used, must in most cases involve reference to oxygen more or less directly, the Committee sees no reason to change the position taken in its Second Report,[3] that no advantage is to be gained by any change of standard at the present time.

Hydrogen.—Although no change in the atomic weight of hydrogen is made in this year's table, it seems increasingly probable from mass spectrographic measurements[4] that the atomic weight of hydrogen is 0.0002–0.0003 higher than the current value. As pointed out by Moles,[5] chemical determinations have ordinarily been made with electrolytic hydrogen which, owing to isotopic separation, has a less than normal proportion of deuterium.

Carbon.—Toral and Moles[6] have determined the density of carbon dioxide, made by pyrolysis of sodium bicarbonate, with the following average results. Individual results are not given.

1 atmosphere	1.97701
$^1/_2$ atmosphere	1.97014

Limiting density is then 1.96327 and the atomic weight of carbon 12.006 if gram molecular volume is taken as 22.4146. Using their own value for the limiting density of oxygen Toral and Moles obtain the value 12.007 for carbon.

Carbon.—Baxter and Hale[7] have determined the atomic weight of carbon by combustion of hydrocarbons. A weighed amount of hydrocarbon was burned in pure oxygen and both the carbon dioxide and the water formed were collected and weighed. From the weight of water the weight of hydrogen was calculated and subtracted from the weight of hydrocarbon to find

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(1) Authors of papers bearing on the subject are requested to send copies to each of the three members of the Committee at the earliest possible moment: Prof. G. P. Baxter, Coolidge Laboratory, Harvard University, Cambridge, Mass., U. S. A.; Prof. O. Hönigschmid, Sofienstrasse 9/2, Munich, Germany; Prof. P. LeBeau, Faculté de Pharmacie, 4 Avenue de l'Observatoire, Paris VI^e, France.

(2) Dole, THIS JOURNAL, **57**, 2731 (1935); *J. Chem. Phys.*, **4**, 268 (1936).

(3) *Ibid.*, **54**, 1269 (1932).

(4) Aston, *Nature*, **135**, 541 (1935); **137**, 357 (1936).

(5) Moles, *Anales soc. españ. fís. quím.*, **33**, 721 (1935).

(6) Toral and Moles, *Bol. acad. cienc. exactas, fís. y nat.*, *Madrid*, **2**, No. 4, 4 (1936).

(7) Baxter and Hale, THIS JOURNAL, **58**, 510 (1936).

THE ATOMIC WEIGHT OF CARBON

Weights in grams							
Sample	H_2O	H	C	CO_2	O	C:O_2	At. wt. C
			Chrysene				
2.78044	1.31209	0.14680	2.63364	9.65247	7.01883	0.375225	12.007(2)
2.69258	1.27609	.14277	2.54981	9.34368	6.79387	.375310	12.009(9)
2.97782	1.41063	.15782	2.82000	10.33447	7.51447	.375276	12.008(8)
2.99649	1.41913	.15877	2.83772	10.39870	7.56098	.375311	12.010(0)
					Average	.375281	12.009(0)
			Triphenylbenzene				
3.00012	1.59012	0.17790	2.82222	10.34136	7.51914	0.375338	12.010(8)
2.99773	1.58730	.17759	2.82014	10.33463	7.51449	.375294	12.009(4)
2.99639	1.58592	.17743	2.81896	10.33026	7.51130	.375296	12.009(5)
					Average	.375309	12.009(9)
			Anthracene				
2.99484	1.51453	0.16945	2.82539	10.35398	7.52859	0.375288	12.009(2)
2.04930	1.03682	.11600	1.93330	7.08554	5.15224	.375235	12.007(5)
					Average	.375262	12.008(4)
					Average of all		12.009(1)

the weight of carbon, from which, with the weight of carbon dioxide formed, the ratio of carbon to oxygen may be calculated.

Hydrocarbons were purified by chemical treatment, by crystallization from hydrocarbon solvents and by distillation or sublimation.

Combustion was effected by slowly evaporating weighed amounts of hydrocarbon into a stream of an excess of oxygen which passed over platinum catalysts in a quartz tube, first at 650°, but eventually at 800°. A short section of copper oxide provided for a possible deficiency of oxygen. Water was collected largely by condensation but partly by phosphorus pentoxide. Carbon dioxide was collected in ascarite (sodium hydroxide) and escape of water from the carbon dioxide absorber was prevented by phosphorus pentoxide. Vacuum corrections are applied.

Results with pyrene were inconsistent and differed from those with other hydrocarbons.

This result is in accord with recent gas density and mass spectrographic evidence that the atomic weight of carbon is not far from 12.01. Accordingly the International value has been altered to this figure.

Batuecas[8] recalculates his data on the densities of several gases and finds values for carbon from 11.999 to 12.007, and for nitrogen 14.011 and 14.009.

Neon.—Jungbluth-Ficht and Hoeppener[9] starting with neon containing 18% of helium, fractionated this gas by adsorption on active charcoal at low temperature. The products of the last three fractionations gave the following densities (volume of globe = 300 ml., g = 980.616)

A	0.8988
B	0.89949
C	0.89990

The density of the purest fraction (C) corresponds to the atomic weight of neon in current use.

Potassium.—Brewer[10] has measured the abundance ratio K^{39}/K^{41} in potassium from various sources. With minerals the ratio varied from 14.11 to 14.32 (except for one sample which gave 14.6). With plant ash a larger variation was found, from 12.63 (kelp) to 14.6 (potato sprouts). In sea water from different localities the ratio was constant at 14.20. The abundance ratio 14.20, with the packing fraction -7.0×10^{-4} and the conversion factor 1.00027, give 39.094 for the atomic weight of potassium. With the average abundance ratio from minerals, 14.25, the atomic weight is 39.093. The abundance ratio corresponding to the atomic weight 39.096 is 13.93.

Gallium.—Lundell and Hoffman[11] have determined the ratio of gallium to gallium oxide. Gallium of 99.999% purity was prepared by a combination of wet methods, electrolysis and fractional crystallization of the metal.[12] By chemical and optical examination the crystals were found to be free from oxide film. In one set of experiments weighed crystals were dissolved in a mixture of nitric, hydrochloric and

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[8] Batuecas, *Bol. Univ. Santiago*, Oct.-Dec., 1935.

[9] Jungbluth-Ficht and Hoeppener, *Ber.*, **68**, 2389 (1935).

[10] Brewer, THIS JOURNAL, **58**, 365, 370 (1936).

[11] Lundell and Hoffman, *Bur. Standards J. Research*, **15**, 409 (1935).

[12] Hoffman, *ibid.*, **13**, 665 (1934).

THE ATOMIC WEIGHT OF GERMANIUM

Fraction	$GeBr_4$, g.	Ag, g.	GeBr:4Ag	At. wt. Ge	AgBr, g.	$GeBr_4$:4AgBr	At. wt. Ge
2	3.57997	3.93852	0.908963	72.572	6.85620	0.522151	72.567
4	7.58115	8.33982	.909030	72.601	14.51750	.522208	72.610
6	4.90761	5.39888	.909005	72.590	9.39827	.522182	72.591
7	6.13136	6.74501	.909022	72.597	11.74160	.522191	72.598
9	4.57465	5.03256	.909011	72.592	8.76096	.522163	72.577
11	8.62179	9.48497	.908995	72.586	16.51123	.522177	72.587
12	6.31559	6.94772	.909016	72.595	12.09440	.522191	72.598
13	6.80706	7.48879	.908967	72.573	13.03664	.522148	72.565
14	5.46488	6.01211	.908979	72.579	10.46570	.522171	72.582
15	6.03550	6.63970	.908996	72.586	11.55892	.522151	72.567
Total	60.01956	66.02812	.909000	72.588	114.94142	.522175	72.586

THE ATOMIC WEIGHT OF GERMANIUM

Fraction	$GeCl_4$, g.	Ag, g.	$GeCl_4$:4Ag	At. wt. Ge	AgCl, g.	$GeCl_4$:4AgCl	At. wt. Ge
1	3.10145	6.24157	0.496902	72.595			
2	2.21830	4.46415	.496914	72.600			
4	3.04473	6.12798	.496857	72.576	8.14193	0.373957	72.579
6	3.45885	6.96104	.496887	72.589			
7	3.06428	6.16679	.496900	72.594			
8	3.47933	7.00214	.496895	72.592			
10	2.75854	5.55169	.496883	72.587	7.37629	.373974	72.589
5	4.26094	8.57525	.496888	72.589			
3	2.95678	5.95028	.496914	72.601	7.90580	.374001	72.605
Total	8.76005				23.42402	.373977	72.591
Total	28.34320	57.04089	.496893	72.591			

sulfuric acids and after removal of nitric and hydrochloric acids gallium hydroxide was precipitated with ammonia. The hydroxide was collected and ignited at 1200–1300° to constant weight (I). In another the gallium sulfate was evaporated to dryness and ignited at 1200–1300° (II). In a third, after solution in mixed nitric and hydrochloric acids, the hydrochloric acid was eliminated by evaporation with nitric acid, the solution of gallium nitrate was evaporated to dryness and the residue ignited at 1200–1300° (III). Oxide samples prepared by the three methods were found to be free from occluded gases. Weights are corrected to the vacuum standard.

THE ATOMIC WEIGHT OF GALLIUM

Method	Ga, g.	Ga_2O_3, g.	2Ga: Ga_2O_3	At. wt. Ga
I	0.86526	1.16307	0.74394	69.730
	1.25888	1.69205	.74400	69.750
	1.23368	1.65815	.74401	69.753
	3.45532	4.64464	.74394	69.727
	2.97452	3.99838	.74393	69.725
		Average	.74396	69.737
II	1.15767	1.55604	.74398	69.745
	1.53230	2.05967	.74395	69.733
	2.48716	3.34320	.74395	69.730
	3.09080	4.15443	.74398	69.741
		Average	.74397	69.737
III	0.78420	1.05411	.74395	69.730
	.80495	1.08196	.74397	69.740
		Average	.74396	69.735
	Average of all		.74396	69.737

The difference between the average value for gallium and that found earlier by Richards and Craig, though the analysis of $GaCl_3$, 69.72, warrants further investigation.

Germanium.—Hönigschmid, Wintersberger and Wittner[13] have determined the ratio of germanium tetrabromide to silver and silver bromide. The tetrabromide was synthesized from spectroscopically pure germanium and pure bromine and was fractionally distilled in exhausted glass systems. Glass bulbs were partially filled with material at various stages of the fractionation. After being weighed the bulbs were broken under sodium hydroxide and the glass was collected for weighing. The solution was then acidified and compared with silver in the usual way. Finally the silver bromide was collected. Weights are corrected to vacuum. Fractions are numbered in the order of decreasing volatility.

Hönigschmid and Wintersberger[14] have determined the ratio of germanium tetrachloride to silver and silver chloride. Germanium was recovered from the tetrabromide analyses by precipitation as hydroxide or sulfide and after conversion to oxide was reduced in hydrogen. The tetrachloride, which was synthesized from the

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(13) Hönigschmid, Wintersberger and Wittner, *Z. anorg. allgem. Chem.*, **225**, 81 (1935).

(14) Hönigschmid and Wintersberger, *Z. anorg. allgem. Chem.*, **227**, 17 (1936).

THE ATOMIC WEIGHT OF RUBIDIUM

Sample	RbBr, g.	Ag, g.	RbBr:Ag	At. wt. Rb	AgBr, g.	RbBr:AgBr	At. wt. Rb
I	3.67283	2.39554	1.53320	85.485			
I	3.27067	2.13320	1.53322	85.488			
II	4.04039	2.63537	1.53314	85.479			
II	3.20309	2.08916	1.53320	85.485			
II	4.00547	2.61245	1.53322	85.488			
II	6.66951	4.35022	1.53314	85.480	7.57272	0.880728	85.481
II	4.69377	3.06150	1.53316	85.481	5.32945	.880723	85.480
II	3.33389	2.17458	1.53312	85.477			
III	3.62456	2.36409	1.53317	85.483	4.11561	.880686	85.473
		Average	1.53315	85.483		.880712	85.478

metal and chlorine prepared from pyrolusite and hydrochloric acid, was fractionally distilled in exhausted systems and collected in sealed glass bulbs. These were analyzed as described above. Weights are corrected to vacuum.

The average result, 72.59, is 0.01 unit lower than the International value, which depends upon the work of Baxter and Cooper.

Rubidium.—Archibald, Hooley and Phillips[15] have redetermined the ratio RbCl:Ag. Rubidium dichloroiodide was fractionally crystallized ten times from dilute hydrochloric acid. Conversion through the sulfate to the hydroxide by means of barium hydroxide was followed by neutralization with tartaric acid and five recrystallizations of the acid tartrate. After conversion of the tartrate to carbonate by ignition, the chloride was formed and recrystallized three times. Spectrographic analysis yielded no evidence of the presence of other alkalies.

Rubidium chloride was prepared for weighing by fusion in nitrogen, and was compared with pure silver by the "standard solution" method of Johnson. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF RUBIDIUM

RbCl, g.	Ag, g.	RbCl:Ag	At. wt. Rb
2.41226	2.15167	1.12111	85.488
2.77942	2.47848	1.12142	85.519
2.90458	2.59105	1.12100	85.476
2.51028	2.23897	1.12118	85.495
3.04508	2.71636	1.12101	85.478
2.25778	2.01411	1.12098	85.474
2.44580	2.18166	1.12107	85.484
2.59528	2.31509	1.12103	85.479
Average of last six analyses		1.12104	85.481

Archibald and Hooley[16] have continued the foregoing investigation by the determination of the ratio RbBr:Ag:AgBr. Rubidium nitrate resulting from the rubidium chloride analyses was freed from silver and converted to acid tartrate which was four times crystallized. Conversion to bromide followed. The first fraction of crystals formed Sample I. The remainder was converted to tribromide and twice recrystallized. The crystals after conversion to bromide formed Sample II, the mother liquors Sample III. Comparison of weighed amounts of rubidium bromide with silver was followed by gravimetric determination of the silver bromide formed. Weights are corrected to vacuum.

The average value from the three ratios, 85.48, is 0.04 unit higher than that found by Archibald over thirty years ago and has been adopted for the table.

Silver.—Hönigschmid and Schlee[17] have determined the ratio of silver nitrate to silver chloride in the dry way. Silver nitrate which had been prepared from the purest silver was crystallized from nitric acid and after being dried in pure air at 150° was fused at 220°. Conversion of the weighed nitrate to chloride was effected, first at 150° in hydrogen chloride diluted with nitrogen, later at higher temperatures in more concentrated hydrogen chloride, until finally the fusion temperature was passed. No loss of silver salt occurred during the conversion. Weights are corrected to vacuum.

THE RATIO OF SILVER NITRATE TO SILVER CHLORIDE

	$AgNO_3$, g.	AgCl, g.	$AgNO_3$:AgCl
	6.60708	5.57445	1.185244
	6.25586	5.27812	1.185244
	6.53756	5.51582	1.185238
	6.42000	5.41662	1.185241
	6.19269	5.22483	1.185242
	7.48847	6.31810	1.185241
	6.58954	5.55968	1.185237
	6.76512	5.70780	1.185241
Total	52.85632	44.59542	1.185241

This experimental value affords close confirmation of International atomic weights which give, as the value to be expected, 1.185235.

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(15) Archibald, Hooley and Phillips, THIS JOURNAL, **58**, 70 (1936).

(16) Archibald and Hooley, THIS JOURNAL, **58**, 618 (1936).

(17) Hönigschmid and Schlee, *Z. angew. Chem.*, **49**, 464 (1936).

THE ATOMIC WEIGHT OF CADMIUM

Sample	$CdCl_2$, g.	Ag, g.	$CdCl_2$: 2Ag	At. wt. Cd
I	3.57277	4.20504	0.849640	112.404
I	4.04302	4.75840	.849659	112.408
I	3.77238	4.43989	.849656	112.407
I	4.07495	4.79598	.849659	112.409
		Average	.849654	112.407
II	4.23323	4.98215	0.849679	112.413
II	4.42435	5.20722	.849657	112.408
II	4.87970	5.74305	.849670	112.411
II	3.43664	4.04470	.849665	112.410
		Average	.849668	112.411
		Average of all	.849661	112.409

$CdBr_2$, g.	Ag, g.	$CdBr_2$: 2Ag	At. wt. Cd	AgBr, g.	$CdBr_2$: 2AgBr	At. wt. Cd
4.13490	3.27717	1.26173	112.399	5.70479	0.724812	112.402
4.07813	3.23214	1.26174	112.402	5.62629	.724835	112.410
4.09476	3.24530	1.26175	112.403	5.64920	.724839	112.411
5.28536	4.18885	1.26177	112.407			
6.12808	4.85675	1.26177	112.407	8.45436	.724842	112.413
	Average	1.26175	112.404		.724832	112.409

Cadmium.—Hönigschmid and Schlee[18] have analyzed cadmium chloride and bromide. Cadmium metal was fractionally distilled in vacuum until spectroscopic examination (Gerlach) showed no impurities. Cadmium chloride was prepared by solution of the metal in nitric acid and displacement of the nitric acid by hydrochloric acid. After crystallization the salt was dehydrated and twice sublimed in hydrogen chloride (Sample I). A second sample was made by heating the metal in dry hydrogen chloride, and twice subliming the product (Sample II). Preparatory to weighing the chloride was fused in nitrogen in a quartz system, since chlorine and hydrogen chloride are retained if the operation is conducted in these gases.

Cadmium bromide was synthesized by heating the metal in a current of nitrogen and bromide in a quartz apparatus and was twice resublimed in nitrogen and bromide before the final fusion in nitrogen. Analysis by comparison with silver followed the conventional lines. Weights are corrected to vacuum.

The average of all the individual values, 112.41, is identical with the present International value and is 0.2 unit higher than Aston's most recent mass spectroscopic determination, 112.2.

Gadolinium.—Naeser and Hopkins[19] have determined the ratio of gadolinium chloride to silver. Samarium–europium–gadolinium material was fractionally crystallized as double magnesium nitrates with and without bismuth as "separating element," and then as simple nitrates with bismuth nitrate as separator. Bismuth was eventually removed as sulfide and the gadolinium was five times alternately precipitated as hydroxide and oxalate. Of the eight final fractions, 7–14, the first six showed only gadolinium in their arc spectra.

Gadolinium chloride was prepared for weighing by evaporating to dryness a solution of the salt in a weighed quartz flask and cautious expulsion of the crystal water wholly by efflorescence, all in a current of hydrogen chloride. Fusion in hydrogen chloride followed. Comparison with silver followed conventional lines, by the equal opalescence method. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF GADOLINIUM

Fraction	$GdCl_3$, g.	Ag, g.	$GdCl_3$: 3Ag	At. wt. Gd
7	0.38265	0.47047	0.81333	156.86
7	.82483	1.01416	.81331	156.85
8	1.56656	1.92608	.81334	156.86
8	0.63482	0.78060	.81325	156.82
9	.68899	.84716	.81330	156.85
9	2.27153	2.79249	.81344	156.89
10	1.89197	2.32637	.81329	156.84
10	1.41902	1.74486	.81326	156.83
11	1.23485	1.51829	.81332	156.85
11	1.61684	1.98796	.81332	156.85
12	1.72986	2.12689	.81333	156.86
12	2.48952	3.06091	.81333	156.85
			.81332	156.85

Since this result is in accord with Aston's recent finding, the value 156.9 has been adopted for the International table.

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[18] Hönigschmid and Schlee, *Z. anorg. allgem. Chem.*, **227**, 184 (1936).

[19] Naeser and Hopkins, THIS JOURNAL, **57**, 2183 (1935).

Erbium.—Hönigschmid[20] has redetermined, by analysis of the chloride, the atomic weight of an erbium preparation containing 0.37 atomic per cent. of yttrium and 0.42% of thulium. The value found was 166.96, which, when corrected for yttrium and thulium becomes 167.24. The material used earlier by Hönigschmid and Kapfenberger, which gave the value 165.2, was found to contain 2.9 atomic per cent. of yttrium, 2.9% of holmium, 2.9% of thulium and 2.7% of ytterbium. Correction for these impurities raises the observed value to 167.35. The discrepancy between the results of Hönigschmid and Kapfenberger, and that of Aston, 167.15, is thus largely removed. However, the Committee feel that it is advisable to defer any change in the value for erbium in the table until the details of Hönigschmid's work are available.

Tantalum.—Hönigschmid and Schlee[21] have continued their work on the atomic weight of tantalum by analysis of tantalum pentachloride. The purification of tantalum material consisted in recrystallization of the double potassium fluoride, conversion to tantalic acid by evaporation with sulfuric acid, extraction of potassium salt with hot water and ignition at 1000°. At this stage, columbium, thorium and zirconium had been eliminated but a trace of iron remained. This was removed by fusion with sodium hydroxide and precipitation of iron as sulfide. Precipitation of tantalic acid with sulfurous acid and ignition followed.

The pentachloride was prepared by first converting the oxide to sulfide by heating in a current of hydrogen sulfide and carbon disulfide and then heating the sulfide in chlorine. Removal of sulfur chloride was effected by distillation in a current of chlorine and by heating in a high vacuum. The product was distilled into small glass bulbs for weighing.

The weighed bulbs were broken under alcohol, and after dilution with water the glass was collected and weighed. Precipitation of tantalic acid with ammonia followed and after addition of a slight excess of nitric acid the solution was compared with weighed quantities of pure silver. Weights are corrected to vacuum.

The average result agrees exactly with that previously found by the authors from the analysis of the pentabromide.

THE ATOMIC WEIGHT OF TANTALUM

$TaCl_5$, g.	Ag, g.	$TaCl_5$: 5Ag	At. wt. Ta
2.59060	3.90135	0.664026	180.891
2.86797	4.31891	.664049	180.903
2.43804	3.67183	.663985	180.869
1.58970	2.39423	.663971	180.861
3.13325	4.71853	.664030	180.893
4.25695	6.41098	.664009	180.883
16.87651	25.41583	.664016	180.885

Lead.—Hecht and Kroupa[22] have determined the atomic weights of several radiogenic leads. Lead chloride from each specimen was purified by crystallization as nitrate, conversion to sulfate and to carbonate, recrystallization as nitrate and as chloride and distillation of the chloride in hydrogen chloride. The ratios of lead chloride to silver and silver chloride were found in the conventional way. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF LEAD

$PbCl_2$, g.	Ag, g.	$PbCl_2$: 2Ag	At. wt. Pb	AgCl, g.	$PbCl_2$: 2AgCl	At. wt. Pb
Pitchblende, Great Bear Lake, N. W. T., Canada						
4.10802	3.19996	1.28377	206.073			
3.10366	2.34736	1.28386	206.090			
3.94641	3.07404	1.28379	206.076	4.08412	0.96628	206.094
3.00540	2.34110	1.28376	206.069	3.11048	.96622	206.075
3.99564	3.11230	1.28382	206.084	4.13520	.96625	206.085
5.21141	4.05947	1.28377	206.071	5.39355	.96623	206.079
Average		1.28379	206.077		.96625	206.083
Uraninite, Wilberforce, Ontario, Canada						
3.05552	2.37910	1.28432	206.190	3.16127	.96655	206.170
3.02424	2.35477	1.28430	206.187			
5.01384	3.90390	1.28432	206.190			
2.57832	2.00763	1.28426	206.178			
Average		1.28430	206.186			
Pitchblende, Katanga, Africa. Black Insoluble						
2.90173	2.26061	1.28360	206.037			
2.77498	2.16174	1.28368	206.053			
Average		1.28364	206.045			
Galena, Tetüche						
3.83794	2.97731	1.28907	207.214	3.95559	0.97026	207.234
4.33839	3.36557	1.28905	207.211	4.47171	.97019	207.213
3.41397	2.64831	1.28912	207.224	3.51904	.97014	207.201
Average		1.28908	207.216		.97020	207.216

The value for Great Bear Lake material is slightly higher than that found by Marble and by Baxter and Alter with a different sample. This difference is undoubtedly due to varying amounts of common lead which the mineral is known to contain. With a different specimen of Wilberforce uraninite Baxter and Bliss found 206.195, although the Th/U ratio of this specimen was lower. It is far from certain, however, that Wilberforce uraninite is free from common lead. The lead in the black insoluble portion of Katanga pitchblende appears to have a slightly higher atomic weight than that in the hydro-

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(20) Hönigschmid, *Naturwissenschaften*, **24**, 619 (1936).

(21) Hönigschmid and Schlee, *Z. anorg. allgem. Chem.*, **225**, 64 (1935).

(22) Hecht and Kroupa, *Z. anorg. allgem. Chem.*, **226**, 248 (1936).

INTERNATIONAL ATOMIC WEIGHTS

1937

	Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.91
Barium	Ba	56	137.36
Beryllium	Be	4	9.02
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.01
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium	Cb	41	92.91
Copper	Cu	29	63.57
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.64
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.002
Holmium	Ho	67	163.5
Hydrogen	H	1	1.0078
Indium	In	49	114.76
Iodine	I	53	126.92
Iridium	Ir	77	193.1
Iron	Fe	26	55.84
Krypton	Kr	36	83.7
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutecium	Lu	71	175.0
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Mercury	Hg	80	200.61
Molybdenum	Mo	42	96.0
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Nitrogen	N	7	14.008
Osmium	Os	76	191.5
Oxygen	O	8	16.0000
Palladium	Pd	46	106.7
Phosphorus	P	15	31.02
Platinum	Pt	78	195.23
Potassium	K	19	39.096
Praseodymium	Pr	59	140.92
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.10
Selenium	Se	34	78.96
Silicon	Si	14	28.06
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.06
Tantalum	Ta	73	180.88
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	184.0
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

chloric acid-soluble portion of the same specimen as determined by Hönigschmid, Sachtleben and Baudrexler, 206.03.

In the light of recent evidence (see preceding reports) the atomic weight of common lead appears to be nearer 207.21 than 207.22 and this change has been made in the table.

Uranium.—Hönigschmid and Wittner[23] have investigated the ratios UCl_4:4Ag:4AgCl and UBr_4:4Ag:4AgBr. Samples of uranium material from different mineral sources were purified by essentially similar methods, including removal of heavy metals with hydrogen sulfide, precipitation of uranyl carbonate and solution in excess ammonium carbonate, crystallization of uranyl nitrate, precipitation of uranyl oxalate and ignition, first to U_3O_8 and then to UO_2 in hydrogen.

The halides were obtained by heating the oxide mixed with sugar charcoal in an atmosphere of nitrogen and chlorine or bromine and the first sublimate obtained was resublimed into a weighed quartz tube, all in a quartz bottling system. In

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[23] Hönigschmid and Wittner, *Z. anorg. allgem. Chem.*, **226**, 289 (1936).

many of the experiments the sublimed halide was fused in an atmosphere of the corresponding halogen before being weighed. Analysis followed by dissolving the salt, oxidizing with hydrogen peroxide in acid solution and comparison with silver. Afterward, in some cases the silver halides were collected. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF URANIUM

UCl_4, g.	Ag, g.	UCl_4: 4Ag	At. wt. U	AgCl, g.	UCl_4: 4AgCl	At. wt. U
Morogoro uraninite						
Sublimed in chlorine and fused in chlorine						
3.08216	3.50091	0.88039	238.077	4.65181	0.66257	238.057
2.17001	2.46488	.88037	238.070			
3.43045	3.89642	.88041	238.087			
Average		.88039	238.078			
Sublimed in chlorine, not fused						
3.43612	3.90301	0.88038	238.072			
4.37836	4.97304	.88042	238.091			
2.90330	3.29784	.88037	238.067			
5.49584	6.24257	.88038	238.074			
4.90768	5.57455	.88037	238.070			
4.99286	5.67158	.88033	238.052			
3.75336	4.26323	.88040	238.084			
4.77701	5.42582	.88042	238.092			
4.47977	5.08841	.88039	238.077			
Average		.88038	238.075			
Katanga curite						
4.63617	5.26634	0.88034	238.056	6.99683	0.66261	238.078
4.36107	4.95357	.88039	238.078	6.58181	.66260	238.069
4.47121	5.07874	.88038	238.073	6.74810	.66259	238.065
Average		.88037	238.069		.66260	238.071
Norwegian euxenite and samarskite						
3.18342	3.61604	0.88036	238.065	4.80457	0.66258	238.062
4.46996	5.07739	.88037	238.068	6.74596	.66261	238.080
4.70546	5.34497	.88035	238.062	7.10206	.66255	238.043
Average		.88036	238.065		.66258	238.062
Sublimed in bromine and fused in bromine						
UBr_4, g.	Ag, g.	UBr_4: 4Ag	At. wt. U	AgBr, g.	UBr_4: 4Ag	At. wt. U.
Morogoro uraninite						
2.42503	1.87618	1.29254	238.091	3.26598	0.74251	238.099
6.09031	4.71214	1.29247	238.064			
5.02670	3.88920	1.29248	238.066	6.77004	.74249	238.084
4.72075	3.65242	1.29250	238.075			
4.69691	3.63391	1.29252	238.085	6.32562	.74252	238.106
4.32567	3.34676	1.29250	238.073	5.82595	.74248	238.078
Average		1.29250	238.075		.74250	238.092
Joaquimstahl pitchblende						
4.78298	3.70053	1.29251	238.081	6.44193	0.74248	238.072
3.49630	2.70491	1.29258	238.108	4.70845	.74356	238.134
2.93547	2.27122	1.29246	238.060			
4.37485	3.38489	1.29246	238.060	5.89220	.74248	238.076
3.02257	2.33852	1.29252	238.082	4.07087	.74249	238.081
3.45769	2.67520	1.29250	238.075	4.65671	.74252	238.104
3.42225	2.64779	1.29249	238.073	4.60899	.74252	238.102
Average		1.29250	238.077		.74251	238.095
Katanga curite						
4.00032	3.09498	1.29252	238.084	5.38767	0.74250	238.087
4.86883	3.76705	1.29248	238.066	6.55730	.74251	238.094
4.35228	3.36732	1.29251	238.078	5.86169	.74250	238.087
4.42009	3.41976	1.29252	238.082	5.95328	.74246	238.062
Average		1.29251	238.078		.74249	238.083
Norwegian euxenite and samarskite						
2.72360	2.10715	1.29255	238.098	3.66815	0.74250	238.090
2.60119	2.01259	1.29246	238.058	3.50361	.74243	238.039
4.20791	3.25555	1.29254	238.098	5.66706	.74252	238.106
Average		1.29252	238.082		.74248	238.078

Within the experimental error there seem to be no differences in the isotopic composition of the samples of uranium, although the original minerals differ considerably in geologic age.

The authors believe the comparisons of the halides with silver to be more accurate than those with silver halides, and point out that, since material fused after sublimation seems to yield slightly higher and less consistent results than when final fusion is omitted, dissociation and loss of halogen may occur during fusion. Therefore they prefer the final value 238.07, which results from analyses of unfused chloride, to the average of all the determinations.

This result is materially lower than the value in use for some time, which depends on the work of Hönigschmid and of Hönigschmid and Schilz. The authors believe the difference to be due to the fact that in the earlier work the halides were finally sublimed and fused in nitrogen before weighing. Since there seems to be no doubt that this is the case, and since the value 238.07 best represents the evidence of the foregoing work, this new value has been adopted for the International table.

Molybdenum and Tungsten.—Hönigschmid and Wittmann[24] and Hönigschmid and Menn[25] have redetermined the atomic weights of molybdenum and tungsten by analysis of the pentachloride and hexachloride, respectively.[26] Their results, Mo = 95.95 and W = 183.92, agree closely with Aston's recent determinations, and are only slightly lower than the International values.

New measurements of doublets by Aston[27] with a perfected mass spectrograph include the following values for certain light isotopes.

O^{16} = 16.0000	(Factor = 1.00025) O = 16.0000
H = 1.00812	H = 1.0079
D = 2.01471	D = 2.0142
He = 4.00391	He = 4.0029
C^{12} = 12.0035	C^{12} = 12.0005
N^{14} = 14.0073	N^{14} = 14.0038

The value for C^{12} is slightly lower than that reported by Aston in 1935, and with an abundance ratio of 1/100 for C^{13} leads to an atomic weight of 12.010.

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[24] Hönigschmid and Wittmann, *Z. anorg. allgem. Chem.*, **229**, 65 (1936).

[25] Hönigschmid and Menn, *ibid.*, **229**, 49 (1936).

[26] Published after Sept. 30, 1936.

[27] Aston, *Nature*, **137**, 357, 613 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Cinchona Alkaloids in Pneumonia. IV. Derivatives of Ethylapocupreine[1]

BY C. L. BUTLER, ALICE G. RENFREW, LEONARD H. CRETCHER AND B. L. SOUTHER

The pneumococcus inhibiting action of various cupreine derivatives and reasons for renewing chemotherapeutic investigations in this field have been given in previous papers of this series.[2,3] In the present paper ethylapocupreine[4] and several of its derivatives are briefly discussed. A preliminary report of the high bacteriostatic activity, high protective action using mice, and lowered toxicity of ethylapocupreine compared to optochin was given at the September, 1934, meeting of the American Chemical Society at Cleveland, Ohio, and discussed in the medical literature[5] by the physicians associated with us. These valuable properties were thoroughly confirmed during the fall and winter of 1934–35. The results are in general agreement with those reported by others[6] although the rather large difference in favor of ethylapocupreine over optochin reported by the Japanese investigators[6b] was not confirmed here. It was later demonstrated by means of a newly developed method using dogs[7] that in large doses this ether as well as optochin had a decidedly damaging effect on the inner ganglionic layer of the retina. Extensive clinical investigation of the drug, therefore, was not carried out. A minor development was the successful use of ethylapocupreine without any unfavorable symptoms in the treatment of pneumococcic infections of the eyes and throat. In this connection the drug is believed to be at least as effective as optochin.

It was believed, on general grounds, and from past experience with hydroxyethylhydrocupreine[2] that the introduction of the hydroxyl group into the ethyl radical of ethylapocupreine would materially decrease its toxicity. The preparation of hydroxyethylapocupreine[8] is not as simple a matter as would at first appear. Ordinary methods, such as alkylation of apocupreine[2,10] in the form of sodium or potassium salt with ethylene chlorohydrin or hydroxyethyl toluenesulfonate yield the desired product but in amounts which are far from satisfactory. Further, the hydroxyethylapocupreine is so contaminated with by-products of uncertain constitution that isolation and purification are tedious and difficult. This result is no doubt due to the presence in the cinchona structure of several reactive groups, other than the phenolic hydroxyl, which is the only point we desire to attack; and to the rather high reactivity of these hydroxyethylating reagents. Various indirect methods such as alkylation of apocupreine N-oxides, and alkylations with toluenesulfonyl esters of glycol monocarboxy esters, either failed completely or gave results so low as to make them impractical.

Equation I

$$\begin{tikzcd}
 & (C_{19}H_{21}ON_2)OCH_2CH_2OCH{=}CH_2 \arrow[d] \\
(C_{19}H_{21}ON_2)OCH_2CH_2OCH_2CH_2Cl \arrow[r, "NaOC_2H_5"] \arrow[ur, "\text{desired}"] \arrow[dr, "\text{obtained}"'] & (C_{19}H_{21}ON_2)OCH_2CH_2OH \\
 & (C_{19}H_{21}ON_2)OCH_2CH_2OCH_2CH_2OC_2H_5
\end{tikzcd}$$

A further attempt consisted in the removal of hydrogen chloride from β-chlorethoxyethylapocupreine with the aim of preparing the vinoxyethyl derivative[2] which should hydrolyze readily to give the desired hydroxyethylapocupreine. However, the only substance which could be isolated under our conditions proved to be the carbitol ether of apocupreine. Equation I shows the desired course of reaction and the one actually obtained.

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(1) Presented before the Medicinal Chemistry Section at the September, 1936, meeting, of the American Chemical Society, Pittsburgh, Pa.

(2) Butler and Cretcher, THIS JOURNAL, **57**, 1083 (1935).

(3) Butler, Nelson, Renfrew and Cretcher, *ibid.*, **57**, 575 (1935).

(4) We have had no desire to ignore the criticisms of the term "apocupreine" made by Henry and Solomon, *Chemistry and Industry*, **54**, 641 (1935). We still believe the name "apoquinine" to be unsuitable for the purified substances isolated from this crude reaction product. In order to avoid further confusion, however, we shall continue to apply the term "apocupreine" only to the purified base of $[\alpha]_D$ $-215°$, until we have the opportunity of going further into the matter of the uniformity of Suszko's base [*Rec. trav. chim.*, **52**, 839 (1933)]. Such opportunity has been denied us up to the present time by the press of more practical matters.

(5) Maclachlan, Permar, Johnston and Kenny, *Am. J. Med. Sci.*, **188**, 699 (1934).

(6) (a) Miura and Okamoto, *Japan J. Med. Sci. IV, Pharmacol.*, **5**, 1 (1930); (b) Ishizaka, Okamoto, Miura and Shako, *ibid.*, **7**, 42, 45 (1933); (c) Matsuda, *ibid.*, **8**, 30 (1934); (d) Gundel and Seitz, *Z. Immunitats.*, **80**, 240 (1933); (e) Leibetruth, *ibid.*, **84**, 445 (1935).

(7) Dawson, Permar, Johnston and Maclachlan, *Am. J. Med. Sci.*, in press.

(8) Protected by U. S. and foreign patents.

Table I

Antipneumococcic Activity and Pharmacological Properties of Ethylapocupreine Derivatives

Drug	*In vitro* inhibits growth in concn. of	Toxicity (20 g. mice). Deaths at dosages of						Protection 20 g. mice. Survivals at dosage of 3 mg.	Visual disturbance (dogs)
		3 mg.	4 mg.	5 mg.	6 mg.	7 mg.	8 mg.		
Optochin	1:800,000	2/30	19/30	30/30	...	...	...	23/30	Positive
Ethylapocupreine	1:800,000	1/30	5/30	22/30	28/30	...	...	23/30	Positive
Hydroxyethylapocupreine	1:400,000	..	...	0/10	1/30	7/30	25/30	21/30	Negative
Butoxyethylapocupreine	1:200,000	..	...	...	25/30	15/15	...	...	Negative
Phenoxyethylapocupreine	1:300,000	2/5	20/20	15/15	...	...	...	...	......

This reaction product proved to have moderate bacteriostatic and protective activity against pneumococcus in mice.

Other special methods of preparing hydroxyethylapocupreine, which we hope may be considerably more useful, are being investigated at present.

As shown in Table I, the expected lowering of toxicity in hydroxyethylapocupreine was accomplished. The bacteriostatic activity of the drug as compared with ethylapocupreine also was diminished considerably. However, the protecting effect when tested against pneumococcus infected mice was maintained at a high level. A further finding of great importance to these investigations was the absence of any unfavorable eye effect in tests by the dog method referred to above.[7] The data shown in Table I as well as results of extensive clinical tests will be reported in detail elsewhere by the medical staff in charge of this phase of the work.

A study of various other alkoxy- and aryloxyethylapocupreines is also in progress. Judging by the examples herein reported, this type of alkylation takes place quite readily on reaction of apocupreine in alkaline alcoholic solution with the desired R-oxyethyltoluenesulfonate. The preparations were undertaken with the two-fold aim of determining their usefulness as pneumococcicidal agents and of investigating their possibilities as intermediates in the preparation of the hydroxyethyl ether.

Butoxyethylapocupreine, as shown in Table I, had moderate activity as a bacteriostatic agent against the pneumococcus. It was rather low in toxicity and showed no eye effect in a small number of trials when tested by the method mentioned above.[7] Phenoxyethylapocupreine also had moderately high bacteriostatic activity. It was, however, more toxic than any cinchona derivative thus far examined. Preliminary attempts at partial hydrolysis of these substances to hydroxyethylapocupreine according to the equation

$$(C_{19}H_{21}ON_2)OCH_2CH_2OR' \longrightarrow (C_{19}H_{21}ON_2)OCH_2\text{-}CH_2OH + R'OH$$

resulted in a complete breakdown of the ethers to apocupreine and presumably glycol and the corresponding alcohol or phenol. Other derivatives which may show a greater difference in stability of ether linkages are also being investigated and will be reported as soon as possible.

Experimental

Ethylapocupreine.—This ether was prepared by alkylation with ethyl *p*-toluenesulfonate or ethyl sulfate, $[\alpha]_D$ −198°.[9] Dihydrochloride from alcohol: $[\alpha]_D$ −237°.[10] *Anal.* Calcd. for $C_{21}H_{26}O_2N_2 \cdot 2HCl$: Cl, 17.2. Found: Cl, 16.8.

Hydroxyethylapocupreine.—Apocupreine in the form of its potassium salt was alkylated in alcoholic solution with one equivalent of ethylene chlorohydrin. The reaction product was worked up as dihydrochloride. On recrystallization from absolute alcohol containing a little ether a pure salt with $[\alpha]_D$ −229° was obtained. The base was recovered from this salt in amorphous condition, $[\alpha]_D$ −194°.

Anal. Base. Calcd. for $C_{21}H_{26}O_3N_2$: C, 71.1; H, 7.4. Found: C, 70.8, 70.6; H, 7.1. *Dihydrochloride.* Calcd. for $C_{21}H_{26}O_3N_2 \cdot 2HCl$: Cl, 16.6; N, 6.6. Found: Cl, 16.2; N, 6.3.

The demonstration of two hydroxyl groups in this substance was accomplished as follows. Two grams of the base was acetylated thoroughly by refluxing with 10 cc. of acetyl chloride for three hours; the base was recovered and again treated with acetyl chloride for two hours. The final amorphous base had $[\alpha]_D$ −51° in absolute alcohol.

Anal. Calcd. for $2CH_3CO$ in $C_{25}H_{30}O_5N_2$: CH_3CO, 19.6. Found: CH_3CO, 20.3, 19.0, 19.1.

β-Chloroethoxyethyl-*p*-toluenesulfonate.—One hundred and twenty-four grams (1 mole) of diethyleneglycol chlorohydrin was heated with 143 g. (0.75 mole) of *p*-toluenesulfonyl chloride in an oil-bath at 142° for ten hours. The product was diluted with benzene and the solution was washed with sodium hydroxide solution. After drying,

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[9] l = 1; c = 1, for all specific rotations herein reported; bases in absolute alcohol, salts in water.

[10] Compare Henry and Solomon, *J. Chem. Soc.*, 1923 (1934).

the benzene was removed under reduced pressure. The yield of oily ester was 130 g. This product proved to be a satisfactory alkylating reagent without any further purification, even though a small sample distilled from a Hickman vacuum still gave low figures when analyzed for sulfur.

Anal. Calcd. for $C_{11}H_{15}O_5SCl$: S, 10.9. Found: S, 9.4, 9.6.

Butoxyethyl-*p*-toluenesulfonate.—This ester was prepared in 74% yield from ethylene glycol monobutyl ether and *p*-toluenesulfonyl chloride in the presence of pyridine by the method which was used in earlier work, for the preparation of ethoxyethyltoluenesulfonate.[2] The product was a heavy oil which could not be distilled readily. It was therefore analyzed after thorough washing and drying.

Anal. Calcd. for $C_{13}H_{20}O_4S$: S, 11.7. Found: S, 11.5.

Phenoxyethyl-*p*-toluenesulfonate.—This reagent was prepared similarly from ethylene glycol monophenyl ether and *p*-toluenesulfonyl chloride by the method described in the earlier paper.[2] The reaction mixture solidified on standing for a short time to a semi-solid crystalline mass which was separated by filtration into a solid and a liquid fraction. The solid material after several recrystallizations from alcohol was obtained in 42.5% yield with melting point 75°.

Anal. Calcd. for $C_{15}H_{16}O_4S$: S, 11.0. Found: S, 10.6.

The rather low yield is due to the fact that *p*-toluenesulfonyl chloride in this case acts, in part, as a chlorinating agent. This was shown by the isolation from the liquid fraction of the reaction product of a 30% yield of β-chloroethyl phenyl ether, m. p. 28°, b. p. 220° (740 mm.). These figures agree with the data given in the literature[11] for this compound.

β-Chloroethoxyethylapocupreine.—Twenty-five grams of apocupreine in form of potassium salt was refluxed in alcoholic solution with 21.7 g. of β-chloroethoxyethyl-*p*-toluenesulfonate for four and one-half hours. The product was worked up in the ordinary way and finally isolated as dihydrochloride; yield 12.5 g. of salt recrystallized from a mixture of alcohol and ether; $[\alpha]_D$ −195°.

Anal. Calcd. for $C_{23}H_{29}O_3N_2Cl{\cdot}2HCl$: Total Cl, 21.7; Cl ion, 14.5. Found: Total Cl, 21.6; Cl ion, 14.4.

Apocupreine Carbitol Ether.—This substance resulted from an attempt to prepare vinoxyethylapocupreine as follows: 4.9 g. (0.01 mole) of β-chloroethoxyethylapocupreine dihydrochloride was added to 30 cc. of absolute alcohol in which 0.75 g. (0.032 mole) of sodium had been dissolved. Sodium chloride was filtered off and the clear solution was heated in a sealed tube for eight hours at 96°. After cooling, a nearly quantitative yield of sodium chloride was filtered off and the alcohol was removed by distillation under reduced pressure. On warming the residue in dilute hydrochloric acid solution for about fifteen minutes, no odor of acetaldehyde could be detected. The product was then worked up as dihydrochloride. Since it could not be obtained crystalline, the salt was purified by several precipitations from alcoholic solution with ether; yield 3.7 g.; $[\alpha]_D$ −183°.

Anal. Calcd. for $C_{25}H_{34}O_4N_2{\cdot}2HCl$: Cl, 14.2; N, 5.6. Found: Cl, 14.3; N, 5.5.

Butoxyethylapocupreine.—Sixty-two grams of apocupreine, alkylated in the usual way with 54.4 g. of butoxyethyl-*p*-toluenesulfonate yielded 38 g. of crude product. Neither the crude base nor the hydrochlorides could be obtained in crystalline condition. The dihydrochloride was therefore partially purified by treating its tepid aqueous solution with nuchar, concentrating to dryness at reduced pressure, and precipitating several times from alcoholic solution with ether $[\alpha]_D$ −198°.

Anal. Calcd. for $C_{25}H_{36}O_3N_2Cl_2$: N, 5.8; Cl, 14.7. Found: N, 5.6; Cl, 14.7.

Phenoxyethylapocupreine.—Sixty-two grams of apocupreine, alkylated with 58.4 g. of phenoxyethyl-*p*-toluenesulfonate, yielded 24 g. of base crystallized from alcohol. A small sample of recrystallized material gave $[\alpha]_D$ −159°, m. p. 178°. The base gave a difficultly soluble dihydrochloride when treated with a slight excess of aqueous hydrochloric acid.

Anal. Base. Calcd. for $C_{27}H_{30}O_3N_2$: N, 6.5. Found: N, 6.4. *Dihydrochloride.* Calcd. for $C_{27}H_{30}O_3N_2{\cdot}2HCl$: Cl, 14.4. Found: Cl, 13.8.

Summary

Ethylapocupreine and several of its derivatives have been prepared. Results of pharmacological tests of importance in chemotherapeutic studies of pneumonia have been presented briefly.

PITTSBURGH, PA.

RECEIVED OCTOBER 31, 1936

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[11] Bently, Haworth and Perkin, *J. Chem. Soc.*, **69**, 165 (1896).

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

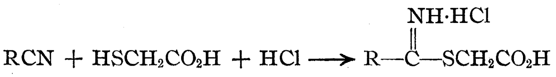
Identification of Nitriles. II. Addition Compounds of Nitriles with Mercaptoacetic Acid

BY F. E. CONDO, E. T. HINKEL, A. FASSERO AND R. L. SHRINER

Nitriles are usually characterized by (a) hydrolysis to the acid, (b) conversion to phenyl alkyl ketones by the action of the Grignard reagent,[1] and (c) formation of the 2,4,6-trihydroxyphenyl alkyl ketone by means of the Hoesch reaction.[2] Each of these methods has some disadvantages, and hence a further search has been made for easily prepared crystalline derivatives.

Nitriles react with alcohols in the presence of hydrogen chloride to form imido ester hydrochlorides. These are good crystalline compounds, but are rather sensitive to moisture, and many of them decompose at or near the same temperature. The analogous thiol compounds obtained by using mercaptans[3] appeared to be more stable. The lower mercaptans are rather disagreeable to use; hence a study was made of other thiol compounds. Thiophenol was found to add to acetonitrile, but the higher nitriles did not readily yield crystalline products.

The best reagent found was mercaptoacetic acid (thioglycolic acid) which readily added to nitriles in the presence of hydrogen chloride, forming α-iminoalkylmercaptoacetic acid hydrochlorides (I),[4] according to the equation



$$\mathrm{RCN + HSCH_2CO_2H + HCl \longrightarrow R{-}\overset{\overset{\displaystyle NH\cdot HCl}{\|}}{C}{-}SCH_2CO_2H}$$

I

By means of this reaction, stable crystalline derivatives could be prepared from both aliphatic and aromatic nitriles in good yields.

The reaction fails in the case of aromatic nitriles containing a group in a position ortho to the cyano group. This result parallels the observations of Pinner,[5] who noted that ortho substituted nitriles failed to form imino ester hydrochlorides when treated with an alcohol and hydrogen chloride.

Since these thioimino ester hydrochlorides are salts, they decompose upon attempting to determine their melting points. It was found, however, that the decomposition temperatures were sharp and reproducible, provided the determinations were made under the same conditions. Table I lists the derivatives of common nitriles, and shows the decomposition points of the compounds when determined by (a) placing the melting point sample in the bath at 20°, and (b) placing the sample in the bath 5° below the decomposition temperature observed by the first procedure.

These thioimino ester hydrochlorides also may be characterized by means of neutral equivalents. Electrometric titrations were carried out, using the glass electrode in order to determine the proper indicator to show the end-point. The curves obtained did not show very sharp breaks corresponding to one or two equivalents of alkali. This appeared to be due to the fact that an appreciable amount of time was necessary to obtain the readings, and so partial hydrolysis or reversal of the addition reaction took place. Hence, titrations were carried out as rapidly as possible, using phenolphthalein, thymol blue and thymolphthalein as indicators. In general, it was found that thymol blue gave the sharpest end-point, and neutral equivalents closely approximating the calculated values for reaction with two equivalents of alkali could be obtained. The data are shown in Table I.

Since many of these ester hydrochlorides decompose at nearly the same temperatures, it is necessary to consider also the boiling point of the nitrile and the neutral equivalent of the derivative in order to have sufficient data definitely to characterize a nitrile.

Previous investigators have shown that thioamides[3b,6] may be alkylated to produce thioimino ester hydrochlorides. In order to establish the

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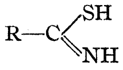
[1] Shriner and Turner, THIS JOURNAL, **52**, 1267 (1930).

[2] Howells and Little, *ibid.*, **54**, 2451 (1932).

[3] (a) Pinner and Klein, *Ber.*, **11**, 1825 (1878); (b) Bernthsen, *Ann.*, **197**, 341 (1879); (c) Autenrieth and Brüning, *Ber.*, **36**, 3464 (1903).

[4] The authors wish to thank Dr. Austin M. Patterson for his help in naming these compounds. They may be named (1) as derivatives of



the enolic form of the thioamide, or (2) as derivatives of mercaptoacetic acid. According to (1) the addition compound from acetonitrile would be "carboxymethyl acetothiimidate hydrochloride," and according to (2) "α-iminoethylmercaptoacetic acid hydrochloride." The latter name seems to be clearer, and is preferable to the former.

[5] Pinner, *Ber.*, **23**, 2917 (1890).

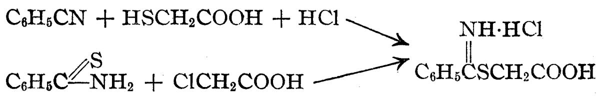
[6] Wallach, *Ber.*, **11**, 1590 (1878).

TABLE I

ADDITION COMPOUNDS OF NITRILES WITH MERCAPTOACETIC ACID

Nitrile		α-Iminoalkylmercaptoacetic acid hydrochlorides						
		Dec. points (corr.)			Neut. equivs.		Chlorine anal., %	
Formula	B. p., °C.	Cold bath	Hot bath	Molecular formula	Calcd.	Found (thymol blue)	Calcd.	Found
CH_3CN	82	114°	115°	$C_4H_8O_2NSCl$	84.7	87.5	20.92	20.93
C_2H_5CN	97	124	128	$C_5H_{10}O_2NSCl$	91.7	93.0	19.32	19.45
n-C_3H_7CN	118	135	137	$C_6H_{12}O_2NSCl$	98.7	99.6	17.95	17.85
i-C_4H_9CN	129	133	137	$C_7H_{14}O_2NSCl$	105.7	106.0	16.76	16.62
n-C_4H_9CN	141	137	138	$C_7H_{14}O_2NSCl$	105.7	105.8	16.76	16.68
i-$C_5H_{11}CN$	155	128	128	$C_8H_{16}O_2NSCl$	112.7	113.0	15.72	15.62
n-$C_5H_{11}CN$	163	136	136	$C_8H_{16}O_2NSCl$	112.7	112.9	15.72	15.69
n-$C_6H_{13}CN$	183	133	133	$C_9H_{18}O_2NSCl$	119.7	119.1	14.81	14.83
n-$C_7H_{15}CN$	200	134	135	$C_{10}H_{20}O_2NSCl$	126.7	126.6	13.99	14.01
C_6H_5CN	191	124	125	$C_9H_{10}O_2NSCl$	115.7	115.5	15.32	15.21
m-$CH_3C_6H_4CN$	214	168	169	$C_{10}H_{12}O_2NSCl$	122.7	122.3	14.44	15.07
p-$CH_3C_6H_4CN$	217	181	182	$C_{10}H_{12}O_2NSCl$	122.7	121.9	14.44	15.16
$C_6H_5CH_2CN$	234	144	146	$C_{10}H_{12}O_2NSCl$	122.7	122.3	14.44	14.34

structure of the compounds prepared in the present work, α-iminobenzylmercaptoacetic acid hydrochloride (II), obtained by the addition of mercaptoacetic acid and hydrogen chloride to benzonitrile, was shown to be identical with that obtained from thiobenzamide and chloroacetic acid.



$$C_6H_5CN + HSCH_2COOH + HCl \rightarrow C_6H_5\overset{\overset{NH\cdot HCl}{\|}}{C}SCH_2COOH \leftarrow C_6H_5C{\overset{S}{\leqslant}}NH_2 + ClCH_2COOH$$

II

Experimental Part

Nitriles.—The aliphatic nitriles were prepared by the action of sodium cyanide on the alkyl halides.[7] The aryl nitriles were made by the Sandmeyer reaction.[8]

α-Iminoalkylmercaptoacetic Acid Hydrochlorides.—Three methods were used in the preparation of the addition compounds. (A) The nitrile and a slight excess of mercaptoacetic acid were mixed together, cooled in an ice-bath and saturated with hydrogen chloride. The tube was stoppered and kept in the ice-bath until crystallization was complete. (B) The nitrile and mercaptoacetic acid were dissolved in an equal volume of absolute ether, the solution cooled in an ice-bath and saturated with dry hydrogen chloride. The tube was stoppered and kept cold until crystallization was complete. (C) The mixture of nitrile (2 g.) and mercaptoacetic acid (4 g.) was treated with 50 cc. of absolute ether, which had been previously saturated with dry hydrogen chloride at 5–10°. The flask was stoppered and placed in a refrigerator until crystallization was complete.

In each case the crystals were removed by filtration and thoroughly washed with absolute ether. They were placed in a vacuum desiccator containing concentrated sulfuric acid, potassium hydroxide and paraffin wax in order to remove the last traces of hydrogen chloride and ether. Procedures (A) and (B) above gave the best yields, 80–90%. The yield depends on the length of time the mixture is allowed to stand. The aliphatic nitriles reacted more rapidly than those of the aromatic series. Crystallization of the addition compound derived from an aliphatic nitrile often started within fifteen minutes, and was usually complete in two to three hours, whereas with the aromatic nitriles the process sometimes required twelve to sixteen hours by procedure (A) or (B) and two to three days when procedure (C) was used. The yields by procedure (C) were lower than by (A) or (B), but the product was of higher purity, and was not sticky and hygroscopic as was sometimes the case when procedure (A) was used. For identification work, procedures (B) and (C) are preferred, and may be used with 0.2 to 0.5 g. of nitrile and proportional amounts of the other reagents, provided care is taken to exclude moisture.

Neutral Equivalents.—An accurately weighed sample was dissolved in 100 cc. of carbon dioxide-free distilled water and *rapidly* titrated with standard, carbonate-free, sodium hydroxide solution, using thymol blue (*p*H change, 8.0–9.6) as the indicator. In the case of derivatives of nitriles containing more than five carbon atoms, it was necessary to dissolve them in 50% alcohol. The end-point was the olive-green color intermediate between yellow and blue. The data are given in Table I.

Analyses.—Although the chlorine in these hydrochlorides is ionic, it was necessary to decompose the compound with sodium peroxide in a Parr bomb, and then determine the chlorine. Direct precipitation of silver chloride by addition of silver nitrate to the thioimido ester hydrochlorides gave erroneous results. In two cases as shown in Table I, namely, the compounds derived from *m*- and *p*-tolunitrile, the chlorine analyses are high. The preparation of these compounds has been repeated many times and various purification processes have been tried. Apparently a small amount of the chlorimide, formed by addition of hydrogen chloride to the nitrile, is occluded by the product, and this results in the high values for chlorine.

α-Iminobenzylmercaptoacetic Acid Hydrochloride.—Equivalent amounts of chloroacetic acid and thiobenzamide were dissolved in absolute ether and the solution allowed to stand for two weeks at room temperature. The crystals which had separated were removed by filtration and triturated with dry acetone. After thorough washing with dry acetone and absolute ether, the crystals decomposed at 124–125°.

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[7] "Organic Syntheses," John Wiley & Sons, New York, 1932, Coll. Vol I, p. 101.

[8] *Ibid.*, p. 500.

Anal. Calcd. for $C_9H_{10}O_2NSCl$: Cl, 15.32; neut. equiv., 115.7. Found: Cl, 15.39; neut. equiv., 115.9.

No depression in the decomposition point occurred when this product was mixed with the compound obtained by the addition of mercaptoacetic acid to benzonitrile in the presence of hydrogen chloride.

Summary

A series of α-iminoalkylmercaptoacetic acid hydrochlorides have been prepared by the addition of mercaptoacetic acid (thioglycolic acid) to nitriles in the presence of hydrogen chloride. These addition products are stable, possess characteristic decomposition points, and may be titrated as dibasic acids by the use of thymol blue as the indicator.

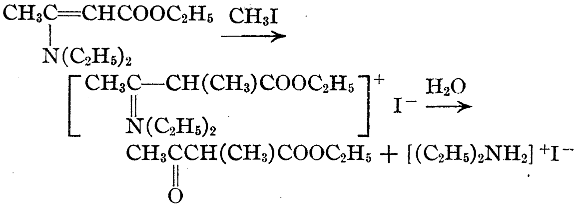
URBANA, ILL. RECEIVED NOVEMBER 16, 1936

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

The Alkylation of Beta-Aminocrotonic Esters

BY WALTER M. LAUER AND GEORGE W. LONES

An important study of the alkylation of ethyl β-diethylaminocrotonate with methyl iodide has led Robinson[1] to formulate the reaction as follows

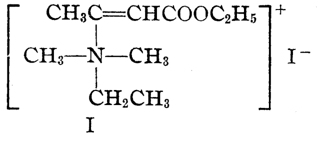


$$CH_3\underset{\displaystyle N(C_2H_5)_2}{\underset{|}{C}}{=}CHCOOC_2H_5 \xrightarrow{CH_3I} \left[CH_3\underset{\displaystyle N(C_2H_5)_2}{\underset{\|}{C}}{-}CH(CH_3)COOC_2H_5\right]^+ I^- \xrightarrow{H_2O} CH_3\underset{\displaystyle O}{\underset{\|}{C}}CH(CH_3)COOC_2H_5 + [(C_2H_5)_2NH_2]^+I^-$$

since diethylammonium iodide and ethyl α-methylacetoacetate were obtained after the reaction mixture was treated with water. An alternative view that the methyl group first attached itself to the nitrogen and subsequently rearranged from the nitrogen to carbon atom is still possible provided the methyl group is assigned a greater migratory aptitude than the ethyl group.

The present work was carried out in order to distinguish between these two mechanisms. The results definitely eliminate the second view and bring additional support to the formulation of Robinson.

Alkylation of ethyl β-dimethylaminocrotonate with ethyl iodide formed a product which on hydrolysis yielded ethyl α-*ethyl*acetoacetate. Now, if the initial step in the process involves the formation of a compound of structure (I)



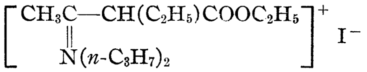
$$\left[\begin{array}{c} CH_3C{=}CHCOOC_2H_5 \\ | \\ CH_3{-}N{-}CH_3 \\ | \\ CH_2CH_3 \end{array}\right]^+ I^-$$

I

and we assign a greater migratory aptitude to the methyl group than to the ethyl group in order to account for the fact that alkylation of ethyl β-diethylaminocrotonate with methyl iodide yields ethyl α-methylacetoacetate, then the expected rearrangement product of I upon hydrolysis would give ethyl α-*methyl*acetoacetate. Instead ethyl α-*ethyl*acetoacetate was obtained.

Likewise, ethyl β-methylaminocrotonate and ethyl β-di-*n*-propylaminocrotonate upon treatment with ethyl iodide followed by hydrolysis yielded ethyl α-ethylacetoacetate. Thus, the substituent which is introduced in the α-position is determined by the alkyl halide used and is independent of the alkyl group or groups already joined to the nitrogen atom.

In the case of ethyl β-di-*n*-propylaminocrotonate it was possible to isolate the ethyl iodide addition product (II)



$$\left[CH_3\underset{\displaystyle N(n\text{-}C_3H_7)_2}{\underset{\|}{C}}{-}CH(C_2H_5)COOC_2H_5\right]^+ I^-$$

II

which upon hydrolysis gave ethyl α-ethylacetoacetate and di-*n*-propylammonium iodide.

Experimental

Ethyl β-aminocrotonate was prepared according to the method of Michaelis,[2] and alkylated with ethyl iodide following the procedure of Collie.[3] After refluxing for twenty hours, a solid which was identified by means of a Volhard titration as ammonium iodide had separated out even though attempts were made to exclude moisture. The reaction mixture, after filtration, was then allowed to stand overnight with 5% sodium hydroxide. After acidification with dilute sulfuric acid, hydrolysis was completed by refluxing. Methyl propyl ketone (identified as the 2,4-dinitrophenylhydrazone, m. p. 141–142°) was obtained upon distillation.

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(1) Robinson, *J. Chem. Soc.*, **109**, 1083 (1916).

(2) Michaelis, *Ann.*, **366**, 337 (1909).

(3) Collie, *ibid.*, **226**, 316 (1884).

Ethyl β-methylaminocrotonate, prepared according to the directions of Kuckert,[4] was heated (100° for twelve hours) with ethyl iodide in a sealed tube. A crystalline solid appeared in the reaction mixture in small amounts. Part of this solid proved to be methylammonium iodide (Volhard titration and preparation of picrate, m. p. 208°). The main portion of the reaction mixture was refluxed with water for fifteen minutes and then allowed to stand overnight. Extraction with ether, after acidification, gave ethyl α-ethylacetoacetate (b. p. 195–198°), which was hydrolyzed to methyl propyl ketone (identified as the 2,4-dinitrophenylhydrazone).

Ethyl β-dimethylaminocrotonate (b. p. 120–121° at 10–11 mm.) was prepared in 66% yield by the action of dimethylamine on freshly distilled ethyl acetoacetate and *alkylated with ethyl iodide* in the following manner.

Ethyl β-dimethylaminocrotonate (15 g.) and ethyl iodide (50 g.) were heated on the steam-bath for forty-five hours. As the reaction proceeded a dark red oily supernatant layer formed. After removal of the excess ethyl iodide by heating on the steam-bath, water (50 ml.) was added and heating was continued for fifteen minutes. The reaction mixture was then cooled, acidified with dilute hydrochloric acid and extracted with ether. Distillation yielded ethyl α-ethylacetoacetate (10.3 g.); b. p. 82–84° at 14 mm.

The ethyl α-ethylacetoacetate was added to 75 ml. to aqueous sodium hydroxide (5%) and allowed to stand for three hours. Dilute sulfuric acid (1:2; 10 ml.) was then added and the mixture was refluxed. A 10-ml. distillate was collected. The upper layer (6.8 ml.), which consisted of methyl propyl ketone, was dried over sodium sulfate and redistilled (b. p. 99–100°). The methyl propyl ketone was characterized by means of its 2,4-dinitrophenylhydrazone (m. p. 140°).

Ethyl β-diethylaminocrotonate prepared in accordance with the directions of Kuckert[4] was alkylated with ethyl iodide. Ethyl α-ethylacetoacetate was obtained in agreement with the results reported by Robinson.[1]

Ethyl β-Di-*n*-propylaminocrotonate.—Di-*n*-propylamine (39 g.) and freshly distilled ethyl acetoacetate (50 g.) were mixed and allowed to stand at room temperature for six weeks. The mixture was then vacuum distilled, collecting the fraction (48 g.) boiling between 149 and 151° at 9 mm.

Anal. Calcd. for $C_{12}H_{23}O_2N$: C, 67.55; H, 10.87. Found: C, 67.65; H, 10.87.

Ethyl β-di-*n*-propylaminocrotonate (25 g.) and ethyl iodide (50 g.) were refluxed on the steam-bath for twenty-four hours. After cooling, the reaction mixture solidified. The solid mass was partially freed of oil by pressing on a porous plate and placing in a vacuum desiccator for one-half hour. The weight of the impure solid was 30 g. One gram of this solid was crystallized by dissolving in absolute alcohol (5 ml.) and adding anhydrous ether until a precipitate just began to form. Cooling in an ice–salt bath caused the separation of fine white crystals (0.56 g.; m. p. 114–116°), which rapidly became yellow on standing in the air.

Anal. Calcd. for $C_{14}H_{28}O_2NI$: C, 45.5; H, 7.6; I, 34.3. Found: C, 45.2; H, 8.0; I, 33.9.

The main portion of the impure solid (25 g.) was then purified in the above described manner and 18.5 g. of crystalline product was obtained.

The salt was then added to water (50 ml.) and boiled for one-half hour. After cooling, acidification with dilute hydrochloric acid, extraction with ether and drying over anhydrous calcium sulfate, a 70% yield of ethyl α-ethylacetoacetate (5.5 g.) was obtained. This ester was again converted to methyl propyl ketone which was identified as the 2,4-dinitrophenylhydrazone; m. p. 141–142°.

The aqueous acid solution from which the ethyl α-ethylacetoacetate had been extracted was concentrated to about one-fourth of its original volume. After cooling in an ice-bath, the solution was made strongly alkaline and extracted with ether. The ether extract, dried over solid potassium hydroxide and distilled, yielded 4 ml. of di-*n*-propylamine (b. p. 108°). The amine was identified as dipropylamine di-propyldithiocarbamate (m. p. 116–117°).[5]

Summary

Several substituted β-aminocrotonic esters were alkylated with ethyl iodide. The results obtained bring additional support for Robinson's views concerning the mechanism of this process.

MINNEAPOLIS, MINN. RECEIVED NOVEMBER 27, 1936

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[4] Kuckert, *Ber.*, **18**, 618 (1885).

[5] Mulliken, "Identification of Pure Organic Compounds," Vol. II, John Wiley & Sons, Inc., New York, 1916, pp. 135–136.

[CONTRIBUTION NO. 46 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Aromatization of Cellulose by Heat

BY R. C. SMITH AND H. C. HOWARD

Graphite is one of the ultimate products of thermal decomposition of all organic substances and thermodynamically can logically be considered the limiting member of the series of aromatic hydrocarbons.[1] Little information is available as to the temperature at which this C_6 ring structure begins to appear when a non-aromatic substance, such as cellulose, is subjected to increasingly severe thermal treatment although the subject is of great theoretical interest in connection with coalification and carbonization processes. Fischer and Schrader[2] regarded the fact that the bituminous coals yield significant amounts of aromatic acids on oxidation as evidence for the point of view that such coals are derived from lignin, since in parallel oxidation experiments on lignin and cellulose, aromatic acids were recovered from the former and not from the latter. Bone[3] confirmed the results of the German workers and reported that in quantitative oxidations with alkaline permanganate, 39–46% of the carbon of three British bituminous coals could be accounted for as benzene carboxylic acids; with cellulose 96.8% of the carbon was found in the simple acids carbonic, oxalic and acetic.[4] Obviously the recovery of aromatic acids by oxidation of coal does not prove that coal is derived exclusively from lignin if it is found that by heating cellulose to temperatures which may conceivably have been reached during coalification, substances are formed which yield aromatic compounds on oxidation.

In the present investigation samples of pure cotton cellulose were heated in a nitrogen atmosphere at temperatures ranging from 190 to 400°. The ultimate composition of the residues from the pyrolyses, with the theoretical composition of cellulose for comparison, are shown in Table I. The high carbon content of the product obtained at 250°, as compared with that at 190°, is very striking. A strong exothermic reaction was observed in this temperature range. The residues from pyrolysis at 190° were light brown in color and fibrous; all the others were black friable chars, but still retained some fiber structure. The gaseous products from a 250° pyrolysis, after correction for nitrogen, consisted of 74.6% carbon dioxide, 11.6% hydrogen, 12.1% carbon monoxide and 1.6% hydrocarbons.

TABLE I

ULTIMATE COMPOSITIONS

	C	H	O (diff.)	Ash[b]
Cellulose, %	44.44	6.17	49.39	..
190° Char[a]	45.34	6.21	47.81	0.64
250° Char	71.54	4.79	22.48	1.19
400° Char	85.58	4.51	9.42	0.49

[a] All chars dried at 100° in vacuum. [b] From corrosion of the bomb.

The residues from the pyrolyses were completely converted to water soluble acidic oxidation products by exhaustive oxidation with alkaline permanganate. The amounts of carbonic, oxalic and volatile acids, the latter calculated as acetic, formed were determined and the percentage distribution of the carbon among the various oxidation products calculated. The results are shown in Table II and data on the oxidation of the original cellulose are included for comparison. The column designated "aromatic carbon" was obtained by difference and gives the percentage of the total carbon in the soluble products unaccounted for by the simple acids, carbonic, acetic, and oxalic. Even in the case of the 250° char, significant amounts of the carbon are not so accounted for. The essentially aromatic character of the carbon assigned to aromatic acids was established by decarboxylation of the mixed acids. Benzene and diphenyl were the only condensable hydrocarbons recovered. With the 250° char the carbon appearing as aromatic acids is less than that found in similar oxidation experiments with a Pittsburgh seam bituminous coal for which an average figure of 30% has been obtained.[5] In the case of the 300° char, however, the aromatic carbon is of the same order as that from the Pittsburgh coal. The 2% "aromatic carbon" reported in the oxidation products of the original cellulose indicates the probable experi-

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(1) Jacobs and Parks, THIS JOURNAL, **56**, 1516 (1934).

(2) F. Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle*, **5**, 208, 551 (1920); F. Fischer, *ibid.*, **8**, 373 (1925–1927).

(3) Bone, Parsons, Sapiro and Groocock, *Proc. Roy. Soc.* (London), **A148**, 521 (1935). The method of determining the carbon reported as "benzene carboxylic acids" was not disclosed.

(4) Bone, Parsons, Sapiro and Groocock, *ibid.*, **A148**, 507 (1935).

(5) Unpublished data.

TABLE II

DISTRIBUTION OF CARBON IN OXIDATION PRODUCTS AND RESULTS OF DECARBOXYLATION

			Carbon					Steam volatile hydrocarbons	
Chars Temp., °C.	Chars Yield, %	$KMnO_4$ g./g. char	Total, g.	Carbonic, %	Oxalic %	Acetic %	Aromatic %	Yield, g.	% to 90°
Original cellulose[a]		6.7	46.9	63.9	32.3	1.7	2.1	..	..
190	89	8.4	43.7	93.7	1.1	0.5	4.7	Trace	..
250[b]	50	12.0	38.6	73.8	11.1	1.5	13.7	1.38	48.9
275	45	11.1	36.2	59.0	14.1	1.8	25.1	2.25	66.8
300	44	10.8	35.4	51.6	18.5	1.6	28.4	2.50	67.5
350	43	10.5	32.7	52.0	12.0	1.8	34.0	1.79	59.3
400[c]	38	10.8	34.3	53.3	12.9	1.0	32.8	4.95[d]	82[e]

[a] 75 g. used, computed on the basis of 100 g. [b] Average of two experiments. [c] Average of three experiments. [d] Three samples decarboxylated together, yield computed for 38 g. of char. [e] To 79.5°.

mental error of the method. The higher recovery of total carbon for cellulose as well as the products of pyrolysis, than calculated, is due to carbonate in the alkali and absorption of carbon dioxide from the air.

The actual recovery of steam volatile hydrocarbons by decarboxylation of the acids from oxidation of the 400° char is somewhat higher than that obtained by decarboxylation of acids from a Pittsburgh seam coal[6] and corresponds to 13 g. per 100 g. of cellulose char. This is equivalent to 5 g. per 100 g. of original cellulose linters.

Densities, d^{25}_4, and refractive indices, $n^{20}_{\rm D}$ of the hydrocarbons recovered from the 250, 275, 300, 350° chars were 0.92, 0.90, 0.91, 0.89, and 1.529, 1.538, 1.522, 1.526, respectively (benzene, d^{25}_4 0.873; $n^{20}_{\rm D}$ 1.501). Fractionation of the hydrocarbons from the 400° char yielded 82%, boiling 78–79.5°, $n^{20}_{\rm D}$ 1.500; 5% crude diphenyl and 13% of tarry residue. Densities and refractive indices prove the hydrocarbons to be aromatic and boiling points indicate a large proportion of benzene.

It is evident that during the thermal decomposition of cellulose, C_6 ring structures are formed rapidly above 200°. While there is wide disagreement as to the temperatures reached in the coalification process,[7] 200–300° appears possible, especially in view of the fact that strong exothermic reactions, such as cellulose exhibits at 150–200°, may have taken place. Hence it follows that the establishment of the presence of aromatic structures in bituminous coals does not necessarily exclude cellulose as a progenitor of such coals.

Experimental

Thermal Decomposition of the Cellulose.—One hundred-gram samples of cellulose linters[8] were packed into a one-liter bomb and flushed with nitrogen. The bomb was electrically heated at a rate of 2° per minute. Temperatures were measured by two thermocouples, one in the center of the bomb and the other between the furnace and the outer wall of the bomb; a temperature gradient of approximately 50° was found, and the temperatures reported correspond to the minimum values observed.

Oxidation and Determination of Carbon Balances.—The dried residue from pyrolysis of 100 g. of cellulose, after vacuum drying at 100°, was suspended in about 2500 cc. of potassium hydroxide solution (140 g. per liter of water) in an iron vessel provided with agitator, cover and reflux condenser. Potassium permanganate was added in small portions over several hours until an excess was present. The vessel was then closed and kept at the boiling point for the period required for discharge of the permanganate, usually several days. The manganese dioxide formed in the reaction was filtered off by suction and thoroughly washed. The combined filtrate and washings, golden yellow in color, were concentrated to less than 2000 cc., cooled, transferred to a 2000-cc. volumetric flask, made up to volume, thoroughly mixed and aliquots withdrawn for determination of the distribution of the carbon. Total carbon was determined in a 5-cc. aliquot by wet oxidation with a chromic–sulfuric acid mixture; carbonic acid in a 10-cc. aliquot by evolution with dilute hydrochloric acid. To determine volatile acids a large aliquot, 100 cc., was diluted to 500 cc., acidified with dilute sulfuric acid and distilled to a small volume. The distillate was titrated with 0.1 *N* alkali using phenolphthalein. To determine oxalic acid a 25-cc. aliquot was made acid with dilute hydrochloric acid, alkaline with potassium hydroxide and finally acid with acetic acid. Calcium acetate was added in excess and the precipitated calcium oxalate, after digestion, was filtered off, washed thoroughly, dissolved in dilute sulfuric acid and the oxalic acid titrated with 0.1 *N* permanganate. Contamination of the calcium oxalate precipitate with the calcium salts of benzene carboxylic acids could have little effect on the oxalate determinations since work on known

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[6] *Cf.* Juettner, Smith and Howard, THIS JOURNAL, **57**, 2324 (1935).

[7] *Cf.* Lewis, *J. Inst. Fuel*, **9**, 235 (1936).

[8] Obtained through the courtesy of Dr. Charles Carpenter Carnegie Institute of Technology.

mixtures of oxalic and benzene carboxylic acids had shown that the former can be titrated quantitatively in the presence of the latter.

Decarboxylation.—Previous work with the oxidation products of coal had indicated the difficulty of recovering in good yields the individual pure aromatic acids present, so recourse was had to decarboxylation as a method of establishing aromatic character.[6] In some cases the solutions remaining, after the aliquots had been removed for analytical work, were concentrated until salts began to separate and placed in the middle compartment of a three-compartment cell, subjected to electrolysis, and the free acids recovered by vacuum evaporation of the anode liquors on the water-bath. The required amount of alkali was added and the decarboxylation carried out as previously described.[9] In other cases the alkali salts were evaporated to a small volume and decarboxylated directly.

Summary

The presence of C_6 ring structures in products obtained by pyrolyzing cellulose at temperatures up to 400° has been established by oxidation followed by decarboxylation and recovery of benzene and diphenyl. The yield of aromatic hydrocarbons, based on the pyrolyzed cellulose, is of the same order as that obtained by similar attack on a Pittsburgh seam bituminous coal. It has been pointed out that the presence of C_6 ring structure in bituminous coal does not exclude the possibility of such coals having been derived from cellulose.

PITTSBURGH, PENNA. RECEIVED DECEMBER 2, 1936

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[9] Ref. 6, page 2326.

[CONTRIBUTION NO. 47 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Oxidation of a Pittsburgh Seam Bituminous Coal and Low Temperature Coke by Alkaline Permanganate

BY B. JUETTNER, R. C. SMITH AND H. C. HOWARD

The present generally accepted picture of the structure of bituminous coal as a system containing condensed rings is based largely on evidence from oxidation experiments.[1] Certain bituminous coals have been reported to yield as much as 46% of their carbon as benzene carboxylic acids on oxidation with alkaline permanganate.[2] Obviously such high yields of one type of compound are of great theoretical interest, and are of possible technical importance.

A study has been made of the nature of the products obtained by exhaustive alkaline permanganate oxidation of a Pittsburgh seam coal[3] and a 500° coke prepared from this coal. It has been found that 90–95% of the carbon of these materials can be recovered after oxidation as a solution of water soluble, non-colloidal acidic products, which vary in color from pale yellow to deep reddish-brown, depending upon the amount of permanganate employed and the oxidation period. Typical data showing the distribution of the carbon[4] among the chief oxidation products are given in Table I. The assumption that the carbon not found as carbonic, oxalic and acetic acids is in aromatic acids, is based upon the fact that the only condensable hydrocarbons recovered by decarboxylation were aromatic and consisted chiefly of benzene and diphenyl. On this basis it is evident that a significant fraction of the carbon in the Pittsburgh coal is in cyclic structures and that coking increases the proportion of cyclic carbon present. However, we have found no evidence that would justify a statement that any considerable fraction of the acids produced by the action of alkaline permanganate on this coal consists of benzene carboxylic acids.

TABLE I

CARBON DISTRIBUTION IN POTASSIUM SALTS

Material		Edenborn coal	500° Edenborn coke
Carbon as	Carbonic acid, %	45.0	40.7
	Acetic acid, %	2.2	1.6
	Oxalic acid, %	15.0	11.6
	Arom. acids (diff.), %	30.8	37.1
Total C recov. as K salts, %		93.0	91.0

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[1] For a review of the work of F. Fischer and co-workers, see Horn, *Brennstoff-Chem.*, **10**, 362 (1929); Bone and co-workers, *Proc. Roy. Soc.* (London), **A110**, 537–542 (1926); **A127**, 480–510 (1930); **A148**, 492–522 (1935). Recent hydrogenation work by Biggs, THIS JOURNAL, **58**, 1020 (1936), constitutes even more convincing evidence.

[2] Bone, Parsons, Sapiro and Groocock, *Proc. Roy. Soc.* (London), **A148**, 521 (1935).

[3] Described in detail in Bur. Mines Tech. Paper 525, 1932.

[4] The general procedure described in ref. 2 has been used. These authors do not reveal the method employed to determine the carbon reported as oxalic and benzene carboxylic acids in their carbon balances.

Recovery and Identification of Acids.—The recovery in good yields of the free acids from their potassium salts presented great difficulties, since all are readily soluble in water and have unfavorable distribution coefficients in solvent systems such as water and ether. The procedure described by Bone, Horton and Ward,[5] the addition of the theoretical amount of sulfuric acid, followed by evaporation to dryness and extraction of the dried residue with ether and acetone, gave poor recoveries and, indeed, on theoretical grounds it is difficult to see why complete metathesis to free acids and potassium sulfate should take place. Two methods have been developed which give satisfactory recoveries of the free acids. They are: (1) acidification of the solution of potassium salts with sulfuric acid followed by extraction of the solution with ether in a continuous extractor of the type described by Kester,[6] and (2) decomposition of the salts by electrolysis in a three-compartment cell. The recoveries of acids obtained by the two methods are illustrated in Table II. The data show that the recovery of the higher molecular weight acids is more complete by electrolysis than by extraction. In confirmation of this it has been observed that while the central compartment in the electrolytic cell ultimately becomes colorless, even very prolonged extraction fails to remove all the color from the aqueous layer in the extraction process. Secondary oxidation of the aromatic acids at the anode during electrolysis appears to be inconsiderable. Because of the high recoveries and the simplicity and convenience of the method, the separation by electrolysis has been used almost exclusively.

TABLE II

COMPARISON OF METHODS OF RECOVERY OF ACIDS

Material	K salts	Acids recov. by elect.	Acids recov. by 78-hr. ether extn.
Carbon as:			
Total, g.	100	45.5	40.7
Carbonic acid, g.	48.5		
Acetic acid, g.	2.3		
Oxalic acid, g.	15.9	13.7 86%	15.6 98%
Arom. acids (diff.), g.	33.3	31.8 96%	25.1 72%

The anode liquors containing the free acids were concentrated in vacuum on the water-bath, but it was found necessary to conduct the final drying operation at not over 50° to prevent discoloration. The acids so recovered are yellow to light buff in color, almost free from inorganic impurities, and completely soluble in water, alcohol and ethyl ether. Since they have all migrated through parchment, the color cannot be due to colloidal or high molecular weight impurities. They contain 30–40% oxalic acid; the carbonic and volatile organic acids are, of course, not recovered. The average yield from Edenborn coal has been 88 g. of these mixed acids per 100 g. of coal; the yield from the coke is higher, 98 g. per 100 g.

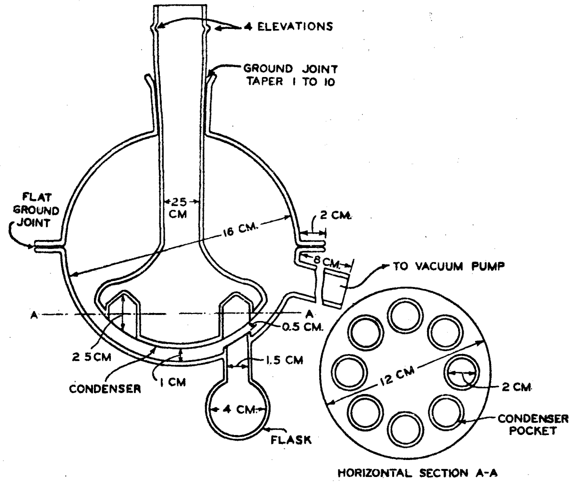

Fig. 1.

The first attempt to isolate pure compounds from the mixed acids was by esterification with diazomethane followed by fractionation in a high vacuum still, Fig. 1. Typical data from such a fractionation are shown in Table III. A significant part of these esters was not distillable even at 300° in a vacuum of 1 micron. From the low boiling fractions considerable amounts of crystalline dimethyl oxalate separated; higher fractions ranged from limpid oils to semi-solid resinous products, and in no case was any pure crystalline material other than dimethyl oxalate recovered. The non-distillable residue was a reddish-brown, brittle resin.

The next attempts at separation were by means of the formation of characteristic salts. By saturation of an aqueous solution of the mixed salts with ammonia at low temperature a copious crystalline precipitate resulted. Mellitic acid precipitates almost quantitatively under these conditions, as a hydrated ammonium mellitate, and a considerable amount of the oxalic acid also separates as the monohydrated ammonium salt. The free acids from the insoluble ammonium salts

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(5) Bone, Horton and Ward, *Proc. Roy. Soc.* (London), **A127**, 489 (1930).

(6) Kester, *Ind. Eng. Chem.*, **24**, 1121 (1932).

Table III

Fractionation of Methyl Esters from Coal

(10.9 g. used)

Bath temp., °C.	Time to constant temp., min.	Time at constant temp., min.	Max. press., microns	Weight of condensate, g.	Nature of condensate
-120	60	75	5.5	1.60	White, crystalline
120–170	25	95	4.9	1.19	Colorless, glassy
170–220	25	95	2.6	2.20	Yellow, glassy, some crystals
220–300	25	60	9.1	0.44	Brown, resinous
		Condenser washings		1.13	
		Total distillate		6.56 g. = 60.2%	

Table IV

Separation of Acids and Fractionation of Esters from Coal

(60.0 g. Acids Used)

	Acids recovered, g.	Esters, g.	Distillate up to 220° g.	Distillate up to 220° %	Methyl esters isolated g.	Methyl esters isolated g. per 100 g. coal
Insoluble ammonium salts	17.5[a]	14.1	11.3	80.0	6.0 oxalic 0.4 mellitic[b]	8.8 0.6
Insoluble calcium salts	3.7[a]	1.8	0.45	25.0	.05 terephthalic	.08
Barium salts:						
A—Water insoluble						
(a) Insol. in acetic acid	10.2	12.5	3.46	27.7	.52 pentacarboxylic	.76
(b) Sol. in acetic acid	10.6	12.6	6.34	50.0	.46 prehnitic (?) .05 pentacarboxylic	.67 .07
B—Water soluble	11.0	13.4	7.15[c]	53.3		
Total	53.0 (88.3%)	54.4	28.7	52.8	7.48	11.0

[a] Large amounts of oxalic acid present, the ester of which is volatile, hence the yield of ester is poor. [b] From the residue, non-volatile at 220°. [c] Liquid at room temperature; no individuals isolated.

were recovered by electrolysis, esterified and distilled. No difficulty was encountered in isolating the pure hexamethyl ester of mellitic acid. The yield of pure ester from the coal was 0.6 g. per 100 g. of coal; from the coke, 0.8 g.

The soluble ammonium salts in the filtrate from the ammonia precipitation were converted to barium salts by excess barium hydroxide and these fractionated into water insoluble and soluble, and the water insoluble barium salts were separated again into two fractions, insoluble and soluble in glacial acetic acid. In the first two experiments separation into an insoluble calcium salt fraction was also made, but this proved of little value and was omitted in later work. The amounts of acids recovered from the different salt fractions, yields of total esters, and pure esters isolated are shown in Table IV. Work with an authentic sample of the methyl ester of benzene pentacarboxylic acid had shown that this ester distilled rapidly in our still at 220° at 1 micron pressure. It had also been observed in the earlier experiments with the esters of acids from coal that temperatures above 220° resulted in little increase in condensate, but considerable thermal decomposition. Accordingly in all later fractionations the maximum temperature used was 220°.

The relatively small proportion of the methyl esters from the coal acids distilling in the range in which authentic samples of the esters of the higher benzene carboxylic acids were known to distil rapidly, led to the conclusion that oxidation had been incomplete. Hence a sample of acids prepared by the oxidation of coke was re-oxidized with further amounts of alkaline permanganate for a two-week period. The permanganate used in the first oxidation was 8.9 g. per g. of coke; in the reoxidation an additional 1.4 g. was necessary. The distribution of the carbon before and after this reoxidation is shown in Table V. It is evident that under these conditions the aromatic acids are attacked. As a result of the further oxidation, the color of the acids in aqueous solution changed from reddish-brown to golden-yellow. There is also definite indication of oxidation of oxalic acid.[7]

Recovery of the acids, fractionation of the acids by salt precipitation and fractionation of

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[7] Bone and co-workers (ref. 2) reported that oxalic acid was not further oxidized by alkaline permanganate.

TABLE V

REOXIDATION OF ACIDS FROM COKE

Material	Orig. acids (22.8 g. oxalic 57.2 g. aromatic)	Reox. acids[a]
Carbon as:		
Carbonic acid, g.		10.47
Acetic acid, g.		0.11
Oxalic acid, g.	6.1	3.38
Arom. acids (diff.), g.	28.0	18.79
Total carbon, g.	34.1	32.75

[a] The reoxidized acids recovered by electrolysis weighed 55.5 g. and contained 12.6 g. oxalic and 42.9 g. aromatic acids.

the esters were carried out substantially as described for the products from coal. The data are collected in Table VI. As was found with the coal, a large fraction of these esters was not distillable at 220° and 1 micron pressure, and the same type of reddish-brown, resinous residue remained in the still. However, significantly greater amounts of hexamethyl mellitate and of the ester of the pentacarboxylic acid were isolated.

TABLE VI

SEPARATION OF ACIDS AND FRACTIONATION OF ESTERS

(50 g. of Reoxidized Coke Acids Used)

	Acids recov., g.	Esters, g.	Distillate up to 220°		Distillable esters — Wt. of fractions and compounds isolated, g.				
			g.	%	−120°	120–170°	170–220°	Washings[a]	Non-vol. residue
Insol. ammonium salts	8.8	10.1	3.13	31	2.77[b]	0.01	0.07	0.28	4.13[f]
Barium salts									
A. Water insoluble									
(1) Insol. in acetic acid	26.8	32.8	16.5	50.4	2.52[b]	6.74[c]	4.21[e]	3.02	13.97
(2) Soluble in acetic acid	2.8	2.8	1.59	57.0	0.70[b]	0.48[d]	0.27[e]	0.15	0.48
B. Water soluble	3.6	Not esterified							
Total	42.0 (84%)								

[a] From the condenser. [b] Almost pure oxalate. [c] Mixed crystals; no individuals isolated. [d] Prehnitate from this fraction. [e] Pentacarboxylate from this fraction; 1.66 g. per 100 g. coke. [f] Mellitate from this fraction; 1.78 g. per 100 g. coke.

Because of the small amounts of definite compounds isolated by the methods described, we were led to the use of a more general means of characterizing these acids. It has been pointed out[8] that decarboxylation to the nuclear hydrocarbons constitutes such a tool, and that method was applied. The average yield of steam volatile hydrocarbons recovered by decarboxylation of the acids from coal was 7.7 g. per 100 g. coal, and from the coke acids, 11 g. The higher yield of aromatic hydrocarbons from the coke is in accord with the previously expressed view that carbonization results in increased condensation to cyclic structures. Fractionation of the hydrocarbons obtained by decarboxylation showed 50–60% to be benzene, identified by boiling point and refractive index; 10–15% boiled between 82 and 150° and was not identified; and from the high boiling residue diphenyl was recovered, in some cases amounting to 20% of the total hydrocarbons. Some diphenyl was always formed in decarboxylation experiments with known benzene carboxylic acids, but usually in small amounts, less than 5% of the total steam volatile hydrocarbons.

There appears little doubt that a significant fraction, 50–60%, of the non-volatile acids formed by alkaline permanganate oxidation of this coal and a 500° coke is aromatic. We have, however, found no evidence that any considerable amount of simple benzenoid acids is present. The persistent color and the failure of a large part of the esters to distil under conditions where the esters of authentic samples of benzene carboxylic acids evaporate rapidly, indicate that we are dealing with acids of more complex structure. Although all attempts to isolate them by specific reactions have failed, it seems probable that ketonic aromatic acids are present. Diphenyl was always recovered from the decarboxylation experiments on the acids from coal in significantly greater amounts than obtained in the work with known benzene carboxylic acids. Failure to isolate hydrocarbons more complex than diphenyl, by heating the acids with alkali to elevated temperatures, is not necessarily decisive evidence for the absence of acids with condensed aromatic nuclei, since the drastic alkali treatment may have resulted in scission of the nuclei of ketonic acids. Bamberger and Hooker[9] showed that a diphenyl carboxylic acid, and ultimately diphenyl, resulted

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(8) Juettner, Smith and Howard, THIS JOURNAL, **57**, 2324, 2326 (1935).

(9) Bamberger and Hooker, *Ann.*, **229**, 102–162 (1885).

from the fusion of a fluorenone carboxylic acid with alkali.[10]

Experimental

Oxidation.—Five hundred grams of the 200 mesh coal or coke[11] was suspended in about 35 liters of approximately 0.4 *N* potassium hydroxide solution, contained in an iron kettle which was provided with good mechanical agitation and heated by a large ring burner. The solid permanganate was added in small amounts over a period of several hours and such an excess used that about twelve hours of boiling was required for the discharge of the color. Under these conditions the coal consumed significantly greater amounts of permanganate than the coke; 11 g. per g. was used for the former and 8.9 for the latter. The ratio of grams of alkali per gram of coal or coke was 1.6.

The precipitated manganese dioxide was filtered off by suction on a 32-cm. Büchner funnel, thoroughly pressed, then returned to the kettle and agitated with a few liters of water. This operation was repeated three times. The combined filtrate and washings, approximately 50 liters, were concentrated until salts began to separate, diluted and then transferred to a volumetric flask of suitable size, 6500 cc. Aliquot portions of this solution were used for carbon balances and for the preparation of the free acids.

Carbon Balances.—Total carbon was determined by oxidation of a suitable sized aliquot, with chromic and sulfuric acids; carbonate carbon, by evolution with hydrochloric acid; volatile acids, by steam distillation, after acidification with dilute sulfuric acid, followed by titration of the distillate with standard alkali using phenolphthalein. Volatile acids were calculated as acetic. Oxalate carbon was determined by precipitation of the calcium salt with calcium acetate from an aliquot which was first acidified with hydrochloric acid, then made alkaline with potassium hydroxide, and finally acidified with glacial acetic acid. The calcium salt so obtained was never pure white in color and, on solution in dilute sulfuric acid and titration with standard permanganate, a much less stable end-point was obtained than with pure calcium oxalate. For this reason it is possible that the figures for oxalate carbon are high. The error is not thought to be appreciable. Experiments with mixtures of oxalic and authentic samples of benzene carboxylic acids showed that the former can be determined quantitatively, in the presence of the latter, by titration in acid solution with standard permanganate.

The difference between total carbon by oxidation with chromic and sulfuric acids, and the sum of the carbon found as carbonate, acetate and oxalate is reported as aromatic.

Recovery of Free Acids.—A suitable amount, 1000 cc., of the solution of potassium salts was placed in the middle compartment of a three compartment cell, such as is used for the purification of colloidal material by electrodialysis,[12] and electrolyzed between an anodic diaphragm of parchment and a cathodic diaphragm of cellophane, using a platinum gauze anode and a copper cathode, until the salts were completely decomposed. The acids were recovered by evaporation of the anode solutions in vacuum on the water-bath and the cathodic solutions, containing the potassium hydroxide formed by decomposition of the salts, were discarded. Anode and cathode compartments were emptied approximately twice every twenty-four hours and fresh distilled water added. At the close of the electrolysis the solution in the middle compartment was colorless and evaporation to dryness showed no significant amounts of inorganic or organic substances. In some cases the cathode liquors were pale yellow, indicating migration or diffusion of organic substances toward the negative electrode. The data of Table II show that the recovery of aromatic carbon is satisfactory.

The acids so recovered were relatively free from inorganic impurities; the residue on ignition was less than 1%. In the dry state they darkened and showed evidence of charring at temperatures as low as 100°; hence while the initial concentration was carried out on the water-bath, the final drying was at 50°. The anhydrous acids so prepared were yellow or tan in color, highly hygroscopic, very soluble in water, and soluble in ethyl ether. Analysis for oxalic acid by the method described showed it to be present in different preparations in amounts varying from 25–35%.

Esterification.—An appropriate amount, 20–40 g., of the mixed anhydrous acids, prepared as above, was dissolved in methyl alcohol or ether and subjected to exhaustive methylation, with diazomethane, by the method of Staudinger and Kupfer.[13] After the methylation the solvent was allowed to evaporate at room temperature and the yellow to reddish-brown sirupy mixture of esters was transferred to the molecular still for fractionation. The addition of silver powder to the sirupy mixture was found to facilitate its transfer to the still and eliminated spattering in the subsequent distillation A considerable part of the dimethyl oxalate was no doubt lost with the ether. After distillation the various ester fractions were removed mechanically as completely as possible from the pockets of the condenser. Any material still adhering to the condenser was removed by washing with acetone, and the amounts so recovered are shown in Table VI. The nonvolatile residue was separated from the silver powder by extraction with acetone. Total recoveries were usually above 90%, except in those cases where dimethyl oxalate was present in large amounts. The various ester fractions were crystallized from acetone and water mixtures and the identity of the pure esters established by analysis and mixed melting point with authentic samples, except in the case of the ester of prehnitic acid. None of this acid or its ester was available.

Decarboxylation.—This was carried out as described elsewhere[8] (p. 2326).

Summary

The exhaustive oxidation with alkaline permanganate of a Pittsburgh seam bituminous coal, Edenborn mine, and of a 500° coke from this coal has been studied. It is shown that 90–95% of the carbon can be recovered as the potassium salts of water soluble, non-colloidal acids. Ap-

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[10] Recently Allen and L. Gilman, This Journal, **58**, 939 (1936), have split diphenylnaphthacenequinone into benzoic and a diphenylnaphthacene carboxylic acid by alkali fusion.

[11] Prepared in a large rotating Fischer retort, heating rate 1.9° per minute; held at 500° for one hour.

[12] A ceramic cell, supplied by Maurice A. Knight, Akron, Ohio, and constructed according to the design of Bradfield, was employed.

[13] Staudinger and Kupfer, *Ber.*, **45**, 505 (1912).

proximately 30 and 35% of the carbon of the coal and coke, respectively, is found as aromatic acids.

It has been shown that good recoveries of oxalic and aromatic acids can be obtained by direct electrolytic decomposition, in a three compartment cell, of the potassium salts resulting from the oxidation. Oxalic plus aromatic acids recovered in this way were 88 and 98 g. per 100 g. of coal and coke, respectively.

Esterification followed by distillation of the esters in a special molecular fractionating still resulted in the isolation of no crystalline material other than dimethyl oxalate. Separation of the acids on the basis of varying salt solubilities, followed by liberation of the free acids from the salt fractions, and esterification and fractionation of the esters, resulted in the isolation of small amounts, usually less than 2 g. per 100 g. of coal or coke, of various benzene carboxylic acids. The presence of a large fraction, approximately 50%, of esters which are not distillable, under conditions where it was shown that the esters of known carboxylic acids distil rapidly, has led to the conclusion that a significant part of the acids from this coal and coke are more complex than benzene carboxylic acids. The persistent yellow color of the acids and low volatility of the esters indicate that they may be condensed aromatic acids containing carbonyl oxygen. It is pointed out that the failure to recover hydrocarbons more complex than diphenyl, by decarboxylation, does not necessarily preclude the possibility of the presence of acids with condensed aromatic nuclei containing carbonyl oxygen, since drastic alkaline decomposition is known to split the nuclei of such aromatic acids.

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The Mechanism of Vinyl Polymerizations[1]

BY PAUL J. FLORY

Nearly all compounds containing non-benzenoid carbon–carbon double bonds are capable of undergoing polymerization when subjected to suitable conditions. High molecular weight polymers may be formed from many such compounds, notable examples of which are styrene, vinyl acetate, acrylic acid and its esters, butadiene, and chloroprene. The closely similar characteristics of the conversion of monomer to polymer in these vinyl polymerizations has led to the conclusion that all of them proceed by essentially the same mechanism.

An abundance of evidence has been accumulated to show that typical vinyl polymerizations are chain reactions.[2,3] Except in the presence of certain polymerization catalysts, it may be assumed that the chain is propagated through the successive addition of monomer molecules to a free radical, *i. e.*

$$---(CH_2{-}CHR)_x{-}CH_2{-}CHR{-} \xrightarrow{+\ CH_2{=}CHR}$$

$$---(CH_2{-}CHR)_{x+1}{-}CH_2{-}CHR{-} \xrightarrow{+\ CH_2{=}CHR}$$

etc.[4,5]

In support of this free radical chain mechanism Taylor and Jones[6] have found that ethylene is polymerized by free radicals released in the thermal decomposition of metal alkyls, and Rice and Sickman[7] induced the polymerization of ethylene with methyl radicals from decomposing azomethane. The mechanisms of the equally important processes of chain initiation and termination have remained more obscure. From the limited experimental results available at the present time it is possible to draw certain general conclusions pertaining to the mechanisms of these processes, and upon the basis of these conclusions the theoretical treatment of the kinetics of vinyl polymerizations presented in the following pages has been developed.

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[1] The term "vinyl polymerizations" is used here to include not only polymerizations of derivatives of vinyl alcohol such as vinyl acetate or vinyl chloride, but all polymerizations involving olefinic double bonds and leading to products of high molecular weight.

[2] Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Univ. Press, Oxford, 1935, p. 444.

[3] Chalmers, THIS JOURNAL, **56**, 912 (1934).

[4] Staudinger and Frost, *Ber.*, **68**, 2351 (1935).

[5] Staudinger, *Trans. Faraday Soc.*, **32**, 97 (1936).

[6] H. S. Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930).

[7] O. K. Rice and Sickman, *ibid.*, **57**, 1384 (1935).

General Discussion

There are two pertinent characteristics of vinyl polymerization which must be accounted for by an acceptable mechanism for the process: the apparent autocatalytic character of the conversion of monomer to polymer, *i. e.*, the increase in rate during the first stage of the process,[8] and the approximate constancy of the average molecular weight during the polymerization.[4,5,9] Dostal and Mark[10] have proposed a mechanism based on two processes, chain initiation brought about by a relatively slow "activation" of monomer, and subsequent rapid successive addition of monomers to the activated molecule as indicated above. It was originally assumed that activated molecules continue to "grow" (add on monomers) indefinitely. More recently Dostal[11] has appended to the equations derived on the basis of this mechanism a correction to allow for an "isomerization" reaction whereby the actively "growing" molecule reverts to an inactive polymer molecule incapable of adding on more monomers. The equations of Dostal and Mark are unnecessarily obscure due to their use of an abstract quantity, the "eigenzeit" ($= {}_0\int^t x \, dt$ where x is the fraction of the material which is monomeric at time t), instead of an explicit expression of time.[12] Although the theories of Dostal predict an increase in rate during the early stages of the polymerization in agreement with experiment, they also predict an increase in the molecular weight during the course of the polymerization, which is not in accord with observation.

Staudinger and Frost[4] conceive of the polymerization process as consisting of the three steps: chain initiation, chain propagation, and chain termination. The latter step, whereby an "active" polymer molecule is "deactivated," is incorporated as one of the main reactions. Schulz[13] concludes that inasmuch as according to this mechanism the average molecular weight must be proportional to the ratio of the rate of chain propagation to the rate of chain termination, the constancy of the average molecular weight throughout the course of the polymerization is to be explained by a constancy in this ratio. From this conclusion he derives size distribution equations which are in agreement with the approximate distribution of sizes which he found experimentally in polyisobutylene. This mechanism offers a satisfactory explanation of molecular weight constancy during the polymerization and of the distribution of molecular sizes, but fails to account for the acceleration of the rate at the outset of the polymerization.[14] Thus, neither the theory of Dostal nor that of Schulz is in satisfactory accord with experiment.

Before attempting to formulate a preferable mechanism, let us examine the facts pertaining to the formation and termination of the polymerization chains. Both the formation and annihilation of free radicals (active centers) in the polymerizing monomer, in the absence of extraneous substances such as (negative) catalysts, is subject to a highly significant restriction, namely, that *the free radicals can be formed or destroyed in pairs only.* For example, the free bond terminus of an "active" polymer molecule may be destroyed through saturation of the free bond with a univalent group or a hydrogen atom, or through the formation of a double bond in place of the free radical end group with concurrent loss of a univalent group or a hydrogen atom. In any case the disappearance of the free bond on the chain molecule would require the appearance of a free radical or hydrogen atom elsewhere. Thus, although the active centers can, in effect, be transferred from one molecule to another, they can be destroyed only in pairs by reaction with each other. Consequently, the destruction of active centers must be bimolecular. Furthermore the rate of destruction of active centers must be proportional to the *square* of their concentration, and the length of a particular chain from initiation to destruction must be inversely proportional to the first power of their concentration.

In photopolymerizations a manifold increase in the rate of production of active centers is brought about without directly affecting the other proc-

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[8] See for example, Mark and Raff, *Z. physik. Chem.*, **B31**, 275 (1936).

[9] It has been found in this Laboratory recently that the average molecular weight of methyl methacrylate polymer at less than one per cent. conversion does not differ significantly from the average molecular weight of the polymer when polymerization is nearly complete.

[10] Dostal and Mark, *Z. physik. Chem.*, **B29**, 299 (1935).

[11] Dostal, *Monatsh.*, **67**, 1 (1935); **67**, 63 (1935).

[12] Gee, *Trans. Faraday Soc.*, **32**, 656 (1936), has simplified the abstract and approximate equations of Dostal and has shown the consequences of chain deactivation mechanisms of several sorts. He has attempted to apply his theories to polymerizations in general without differentiating between the various types [Carothers, *Chem. Rev.*, **8**, 378 (1931)] which involve unlike mechanisms. See Gee and Rideal, *Trans. Faraday Soc.*, **31**, 969 (1935), and **32**, 666 (1936).

[13] Schulz, *Z. physik. Chem.*, **B30**, 379 (1935).

[14] Schulz has mentioned in a footnote that perhaps an occasional "branching" of the chain to bring about initiation of one or two new chains at the moment of deactivation might explain the acceleration in rate.

esses involved. With the resultant increase in the concentration of active centers the chain length must decrease and so, according to the conventionally accepted identity of chain length and degree of polymerization, a decrease in molecular weight would be expected. In conflict with this latter deduction, photopolymerized methyl methacrylate[20] (methyl α-methyl acrylate) is not of appreciably lower molecular weight than polymer prepared in the absence of light at the same temperature. Staudinger and Schwalbach[15] obtained their highest molecular weight polyvinyl acetate by photopolymerization at 20°. Although no polymer was prepared by thermal polymerization at this temperature, extrapolation of data at higher temperatures (*cf. seq.*) indicates approximate equality of the molecular weights of photo and thermal polymers at 20°. Staudinger and Schwalbach also found that introduction of oxygen retarded the rate of the photopolymerization much more than it reduced the molecular weight.

It is evident from these results that an increase in the number of active centers does not decrease the molecular weight, nor does impedance of the reaction through the destruction of active centers by a negative catalyst necessitate a corresponding reduction in molecular weight. These facts suggest that the reaction which limits the growth of a particular molecule, *i. e.*, the reaction which determines the molecular weight, and the reaction which destroys active centers are not one and the same reaction, but are entirely independent processes. This concept has been embodied in the following scheme for the mechanism of vinyl polymerizations

$$M_1 + M_1 \longrightarrow 2M^* \qquad (1)$$
$$M^*_n + M_1 \longrightarrow M^*_{n+1} \qquad (2)$$
$$M^*_n + M \longrightarrow M_n + M^* \qquad (3)$$
$$M^*_n + M^*_m \longrightarrow M_n + M_m, \text{ or } M_{n+m} \qquad (4)$$

where M_1 denotes a monomer molecule, M_n a polymer molecule composed of n units, and M a molecule containing an unspecified number of units; a molecule bearing an active center is marked with an asterisk. Reaction (1) has been written to imply the simultaneous formation of two active centers; as will be shown later, both of them are very probably on the same molecule (dimer or trimer). The active centers created in (1) undergo the chain propagation reaction (2) repeatedly until at some stage the "chain transfer" reaction (3) intervenes, whereupon the polymer molecule loses the active center and ceases to grow. The molecule M* which inherits the active center grows by the repeated occurrence of reaction (2) until (3) again intervenes, etc. At a favorable collision of two of the active centers, which will be relatively rare since the active centers must be present in such minute concentrations, mutual deactivation (4) will occur. The production of each active center will, on the average, bring about the formation of many polymer molecules before the effect of the active center is finally ended by reaction (4). (It is assumed that the absolute rate of (3) is much greater than that of (4).)

The principal feature of the above mechanism in contrast to previous theories is the concept of distinctly separate processes for the interruption of the growth of a particular molecule and for the destruction of active centers. As the following discussion shows, this mechanism is capable of explaining in a quantitative manner the acceleration of the rate which occurs at the outset of the polymerization, the approximate constancy of molecular weight during the course of the process, and the molecular weight dependence on temperature and independence of rate of polymerization.

Kinetics of Conversion of Monomer to Polymer

The following analysis of polymerization kinetics will be restricted to non-catalytic and homogeneous processes, *i. e.*, to polymerizations carried out under catalytically aseptic conditions. It will be assumed that the rate constants of reactions (2), (3) and (4) are independent of the size of the polymer molecule bearing the active center. Hence, the probability either of chain transfer or of chain termination at any particular stage of growth of the polymer will be the same as for any other stage of growth. If the molecular weight of the polymer is disregarded and only the conversion of monomer to polymer is considered, then reactions (1), (2) and (4) will suffice as a basis for a kinetic interpretation of the process. As discussed above, it is apparent that both (2) and (4) must be second-order processes. Chain initiation (1) cannot be first order (in the absence of catalysts) because as shown in a following section the energy requirement for such a process is too great, but it may be either second or third order. In the following treatment (2) and (4) will be taken as second order, and equations will be derived for both a second order and a third order initiation process.

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(15) Staudinger and Schwalbach, *Ann.*, **488**, 8 (1931).

Polymerization Kinetics Assuming Second Order Chain Initiation.—The following notation will be used

n = concentration of monomer
N = concentration of active centers
k_1, k_2 and k_4 = velocity constants of reactions (1), (2) and (4), respectively.

If (1), (2) and (4) are all second order[16]

$$\mathrm{d}N/\mathrm{d}t = k_1n^2 - k_4N^2 \qquad (5)$$

$$\mathrm{d}n/\mathrm{d}t = k_2Nn \qquad (6)$$

Dividing equation (5) by (6), integrating and supplying the boundary condition, $N = 0$ when $n = n_0$, gives

$$N = \left(\frac{k_1}{k_4 - k_2}\right)^{1/2} [n^2 - n_0^2(n/n_0)^{2r}]^{1/2} \qquad (7)$$

where $r = k_4/k_2$. Substituting (7) in (6) and letting $n/n_0 = x$ and $n_0(k_1k_2)^{1/2} = K$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -Kx^2\left(\frac{1 - x^{2r-2}}{r - 1}\right)^{1/2} \qquad (8)$$

Equation (8) and some of the equations derived therefrom are indeterminate at the point $r = 1$.

The relation of x, the fraction of the original material which is unpolymerized, to t is completely determined according to (8) by two parameters, K and r. Since K occurs conjugate with t, a change in K merely has the same effect as an alteration of the time units; the fundamental characteristics of the variation of x with t are entirely determined by r. The solid curves in Fig. 1A represent solutions of (8) for the several values of r indicated above each curve, time being expressed in arbitrary units equal to $1/K$; in Fig. 1B a magnified scale has been used to show the initial portions of the curves. Inasmuch as no general solution of (8) has been obtained, these solutions have been obtained by the special methods discussed in the following paragraphs.

When $r = 0$, *i. e.*, when no destruction of active centers occurs ($k_4 = 0$), the mechanism presented above and the original Dostal and Mark[10] mechanism in which second order chain initiation is assumed are identical with respect to conversion of monomer to polymer (although the two mechanisms predict different molecular weights). In this case (8) becomes[17]

$$\mathrm{d}x/\mathrm{d}t = -Kx(1 - x^2)^{1/2} \qquad (8.1)$$

Integration of (8.1) gives

$$\ln\,[(1 + \sqrt{1 - x^2})/x] = Kt \qquad (9.1)$$

The $r = 0$ curve in Fig. 1A was obtained from equation (9.1), which corresponds to Dostal and Mark's[10] approximate equation (20). As they have shown, the rate of polymerization accelerates, reaches a maximum corresponding to the inflection in the curve, and then decreases continuously.

As r increases to large values, *i. e.*, as the rate of destruction of active centers becomes relatively more rapid, the duration of the rate acceleration period becomes shorter, and when $r \gg 1$, (8) approaches the simple second order equation[18]

$$\mathrm{d}x/\mathrm{d}t = -(K/r^{1/2})x^2 \qquad (8.2)$$

For $r = 2$, an intermediate case between these two extremes, equation (8) integrates to

$$Kt = (1 - x^2)^{1/2}/x \qquad (9.3)$$

from which the $r = 2$ curve has been derived. The curves for $r = 10$, 25 and 100, have been obtained by graphical integration using the first form of the equation

$$Kt = 1/2\,(r - 1)^{-1/2}\int_1^x \frac{1}{x}\,\mathrm{d}\ln\left[\frac{1 + (1 - x^{2r-2})^{1/2}}{1 - (1 - x^{2r-2})^{1/2}}\right]$$
$$= (r - 1)^{1/2}\int_1^x (1 - x^{2r-2})^{-1/2}\,\mathrm{d}(1/x)$$

for values of x near unity and the second form for all smaller values of x.

All of the curves meet at sufficiently small $1-x$ values, as shown in Figs. 1A and 1B. An increase in r retards the conversion and brings the inflection point, or point of the maximum rate, to a lower $1-x$ value; that is, a recession in the acceleration period occurs when r is increased.

The relation of x_m, the value of x at the inflection, to r can be derived from (8) as follows

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = \frac{K^2x^3}{(r - 1)}\,[2 - (r + 1)x^{2r-2}] = 0$$
$$x_m = ((r + 1)/2)^{1/(2-2r)} \qquad (10)$$

Curve 2 of Fig. 2 expresses this relation graphically. Substituting (10) in (8) in order to obtain the rate at x_m

$$\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{\mathrm{max.}} = -Kx_m^2\,(r + 1)^{-1/2} = \frac{-K}{\sqrt{2}}\left(\frac{2}{r+1}\right)^{(r+1)/(2r-2)} \qquad (8.8)$$

From a plot of experimental x *vs.* t data, both x_m and $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{max.}}$ can be determined. The value of r may be obtained by substituting x_m in (10), or by the use of Curve 2 in Fig. 2. Equation (8.8) can then be used to evaluate K from r and $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{max.}}$. Exact location of the inflection

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(16) The term $-k_1n^2$, which represents the rate of consumption of monomers by reaction (1), has been omitted in (6). Except when the chain length is very short, this term is negligible compared with $-k_2Nn$.

(17) Equation (8.1) could have been derived directly from (5) and (6) by placing $k_4 = 0$ in the former.

(18) Equation (8.2) is the solution of (5) and (6) for the "steady state" condition $(\mathrm{d}N/\mathrm{d}t) = 0$.

point will, in general, be subject to a large uncertainty, although $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{max.}}$ may be determined quite accurately. When x_m is sufficiently near unity, *i. e.*, when r is large, the following approximate equation can be used satisfactorily.

$$\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{\mathrm{max.}} = -\frac{K}{r^{1/2}} = -n_0k_1^{1/2}\,k_2/k_4^{1/2} \qquad (8.9)$$

Although determination of r $(=k_4/k_2)$ and K $(=n_0(k_1k_2)^{1/2})$ is feasible, evaluation of the individual velocity constants from experimental determination of the course of the polymerization is impossible.

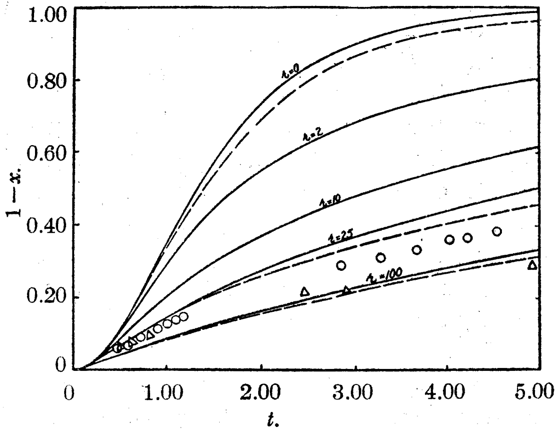

Fig. 1A.—Extent of polymerization *vs.* time for various values of r. Solid curves represent polymerization when chain initiation is second order with time expressed in units of $1/K$; dashed curves represent polymerization when chain initiation is third order, with t in units of $1/K'$. ○, experimental points for the polymerization of 60% vinyl acetate in toluene at 100.9°[19] △, experimental points for 22.5% styrene in toluene at 98.2°.[8]

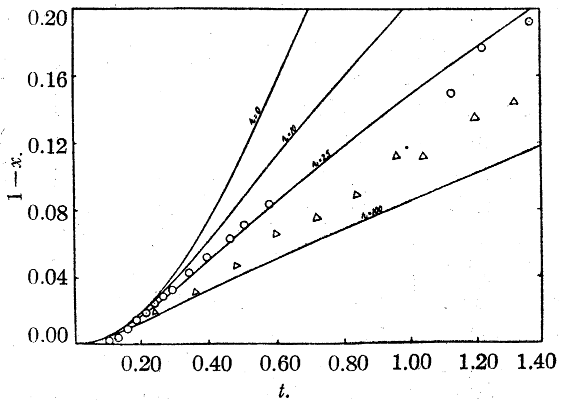

Fig. 1B.—Initial portions of curves shown in Fig. 1A. These are equally applicable to polymerization with second order chain initiation (t in $1/K$ units) or with third order chain initiation (t in $1/K'$ units). ○, 60% vinyl acetate in toluene at 81.8° [19]; △, undiluted styrene at 98.2°.[8]

Polymerization Kinetics Assuming Third Order Chain Initiation.—If reaction (1) is third order, equation (5) must be replaced by

$$\mathrm{d}N/\mathrm{d}t = k_1n^3 - k_4N^2 \qquad (11)$$

Solving (11) and (6) simultaneously gives

$$\mathrm{d}x/\mathrm{d}t = -K'x^{5/2}\left(\frac{1-x^{2r-3}}{r-3/2}\right)^{1/2} \qquad (12)$$

where $r = k_4/k_2$ as before, and $K' = n_0^{3/2}(k_1k_2)^{1/2}$. This equation closely resembles (8); x^2 in (8) has been replaced by $x^{5/2}$, the quantities in parentheses in the two equations differ only slightly, and n_0 in the K in (8) has been replaced by $n_0^{3/2}$ in K'. When r assumes large values (8) approaches a simple second order equation, whereas (12) approaches a five-halves order equation.

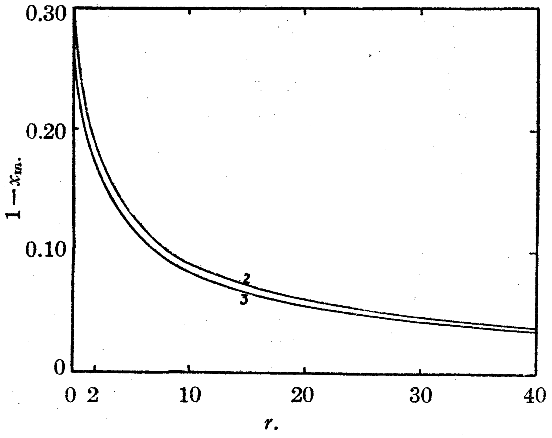

Fig. 2.—Relation of x_m, the value of x at $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{max.}}$, to r for second order initiation (curve 2) and for third order initiation (curve 3).

Several integrals of (12) are shown by the dashed curves in Fig. 1A. Each of these for values of x sufficiently near unity merges with the solid curve for the same r value; in the region shown in Fig. 1B the two sets of curves are substantially identical.

The $r = 0$ curve has been obtained from an integral solution of (12). The other curves have been obtained by the graphical evalution of the integrals in the equation

$$K't = 1/2\,(r-3/2)^{-1/2}\int_1^x x^{-3/2}\,\mathrm{d}\ln\left[\frac{1+(1-x^{2r-3})^{1/2}}{1-(1-x^{2r-3})^{1/2}}\right]$$
$$= 2/3\,(r-3/2)^{1/2}\int_1^x (1-x^{2r-3})^{-1/2}\,\mathrm{d}(x^{-3/2})$$

the first integral being used for x values very close to unity, and the second for all smaller x values.

The relation of x_m to r, obtained by differentiating (12) and equating to zero, is

$$x_m = [2/5\,(r+1)]^{1/(3-2r)} \qquad (14)$$

A comparison of the graph of (14), curve 3 of Fig. 2, with the graph of (10), curve 2 of the same figure, emphasizes the similarity of the two equations. The equation analogous to (8.8) for the maximum rate, obtained by substituting (14) in (12), is

$$(\mathrm{d}x/\mathrm{d}t)_{\text{max.}} = -K'x_m^{5/2}(r+1)^{-1/2} \qquad (12.8)$$

When r is large, $x_m \cong 1$, and

$$(\mathrm{d}x/\mathrm{d}t)_{\text{max.}} = -K'/r^{1/2} = n_0^{3/2}k_1^{1/2}k_2/k_4^{1/2} \qquad (12.9)$$

which is the same as (8.9) except for a factor $n_0^{1/2}$. Using (12.8) or (12.9) K' can be determined from a graph of x *vs.* t in the same manner as was discussed in connection with the corresponding equations in the preceding section. In view of the similarity of the two sets of equations, this method can be used for satisfactory evaluations of r and of K or K' without distinguishing the order of (1), unless r is of the order of unity or less.

Equations have been worked out according to the above methods assuming first order chain initiation, in which case the mechanism becomes the same as assumed by Gee.[12] They too are similar to the equations for second order initiation. Thus, the character of the conversion of monomer to polymer is only slightly dependent upon the order of reaction (1). The kinetic orders of (2) and (4) are highly important, however, in determining the character of the conversion kinetics.

As mentioned before, the above treatment is intended for application to strictly non-catalytic polymerizations only. In general, catalysts may either accelerate reaction (1), ("positive" catalysts) or reaction (4) ("negative" catalysts or inhibitors), or both. If the action of the catalyst is limited to acceleration of (1), the above treatment can be expected to apply, although the order of (1) may be altered. If the catalyst causes chain termination, a term should be added to equation (5), or (11), and the polymerization kinetics will be materially affected. Nearly all catalysts (O_2, Na, $SnCl_4$, etc.) which are known to accelerate the polymerization are also effective chain terminators; the converse is not true.

Application to Experimental Data

Most of the experimental data pertaining to vinyl polymerization kinetics quoted in the following pages has been taken from one of the three following sources: the results of Starkweather and Taylor[19] on vinyl acetate, Mark and Raff's[8] results on styrene, and the work of Starkweather, Flory and Carothers[20] on methyl methacrylate. Starkweather and Taylor using a specially refined technique to prevent contamination (and using Pyrex glass) obtained consistently reproducible results on vinyl acetate. Mark and Raff's results on styrene were also quite reproducible, but the results referred to above on methyl methacrylate were erratic. In a study of catalysis of vinyl polymerizations, Breitenbach and Raff[21] found that, under their experimental conditions (using Jena or soft glass), the polymerization of acrylic ester definitely was catalyzed by the walls of the container, vinyl acetate was subject to the catalysis to a lesser extent, and styrene was free from catalysis. Irreproducibility seemed to accompany catalysis. Considering the reproducibility of the results referred to above on vinyl acetate, the polymerization results for this substance, as well as the results for styrene, must have been substantially free from the effects of catalysis. The polymerization of methyl methacrylate was probably catalytic.

In Figs. 1A and 1B representative experimental data on styrene and vinyl acetate have been included for comparison with the family of theoretical curves. Time units have been adjusted by a factor arbitrarily chosen to bring about the best possible fit with the curves. Considering the likelihood of accompanying secondary effects not taken into account by the simple theory given here, exact agreement with the theoretical curves is not to be expected. It is particularly significant that the theory describes satisfactorily the course of the polymerization during the acceleration period (Fig. 1B), which is so characteristic of most vinyl polymerizations. Although the points are more nearly in agreement with a third order chain initiation (dashed curves in Fig. 1A), a choice between the two mechanisms is scarcely justified by these results alone.

When, as in the case of the polymerization of indene,[22] the acceleration period is apparently absent, the theory leads to the conclusion that r is very large.

Apparent Energies of Activation.—Regardless of whether reaction (1) is second or third order, $(\mathrm{d}x/\mathrm{d}t)_{\text{max.}}$ is proportional, according to (8.9) and (12.9), to $k_1^{1/2}k_2/k_4^{1/2}$ to a satisfactory approximation when r is sufficiently greater than unity. Upon

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[19] Starkweather and G. B. Taylor, THIS JOURNAL, **52**, 4708 (1930). Drs. Starkweather and Taylor have kindly furnished the author with a detailed report of their results.

[20] Starkweather, Flory and Carothers, as yet unpublished.

[21] Breitenbach and Raff, *Ber.*, **69B**, 1107 (1936).

[22] Mark and Raff, *Z. physik. Chem.*, **B32**, 417 (1936).

substituting an Arrhenius expression, $k = Ae^{-E/RT}$, for each velocity constant

$$\log_{10}(\mathrm{d}x/\mathrm{d}t)_{\max.} = B - E_a/2.303RT \qquad (15)$$

where B is a constant containing the A's and E_a is the "apparent energy of activation" defined by

$$E_a = 1/2\,E_1 + E_2 - 1/2\,E_4 \qquad (16)$$

E_1, E_2 and E_4 denoting the activation energies of (1), (2) and (4), respectively.

The $(\mathrm{d}x/\mathrm{d}t)_{\max.}$ values in Table I for styrene, vinyl acetate and methyl methacrylate at various temperatures have been evaluated graphically from plots of experimental data. The data in Figs. 1A and 1B show that at least for styrene and vinyl acetate r is large enough (between 25 and 100) to permit assumption of the proportionality relation upon which (15) is based. In Fig. 3, $\log_{10}(\mathrm{d}x/\mathrm{d}t)_{\max.}$ is shown to be a linear function of $1/T$ in agreement with (15). E_a values given in Table I have been calculated from the slopes of the lines in the figure. For styrene and vinyl acetate they are nearly the same, but E_a for methyl methacrylate is much lower.

TABLE I

MAXIMUM RATES OF POLYMERIZATION AND APPARENT ENERGIES OF ACTIVATION

Substance	Temp., °C.	$(\mathrm{d}x/\mathrm{d}t)_{\max.}$ in min.$^{-1}$ × 10^4	$\log_{10}$ $(\mathrm{d}x/\mathrm{d}t)_{\max.}$	$1/T \times 10^3$ (T, °K.)	E_a, kcal.
Styrene[a]	60	0.211	−4.676	3.000	
Styrene[a]	70	0.494	−4.306	2.914	
Styrene[a]	80	1.64	−3.785	2.832	22.1 (±2)
Styrene[a]	98.2	4.90	−3.310	2.693	
Styrene[a]	130	34	−2.47	2.518	
22.5% styrene[a] in toluene	98.2	2.80			
Vinyl acetate[b]	81.8	8.9	−3.051	2.818	
Vinyl acetate[b]	100.9	46.7	−2.331	2.675	23.1 (±1)
Vinyl acetate[b]	111.2	112	−1.951	2.604	
60% Vinyl acetate[b] in toluene	81.8	5.82	−3.235	2.818	
	100.9	27.5	−2.560	2.675	22.3 (±1)
	111.2	56.0	−2.252	2.604	
Methyl methacrylate[c]	100	4.0	−3.398	2.681	
	132	10.7	−2.970	2.469	10.3 (±3)
	210	91	−2.041	2.070	

[a] The rates for styrene are based on the data of Mark and Raff. [b] The rates for vinyl acetate have been evaluated from the unpublished detailed measurements of Starkweather and G. B. Taylor.[19] [c] Unpublished work carried out by Starkweather, Flory and Carothers.[20]

Chain Lengths and Degree of Polymerization.—According to the proposed mechanism of polymerization two chain lengths must be differentiated: (ν, the average number of monomers caused to polymerize by one active center from its creation in reaction (1) to its annihilation by (4), and λ, the average number of monomers added to a particular chain free-radical from its formation by either (1) or (3) until its growth is arrested by chain transfer (3). According to the present theory many polymer molecules are formed for each active center created and so $\nu >> \lambda$.

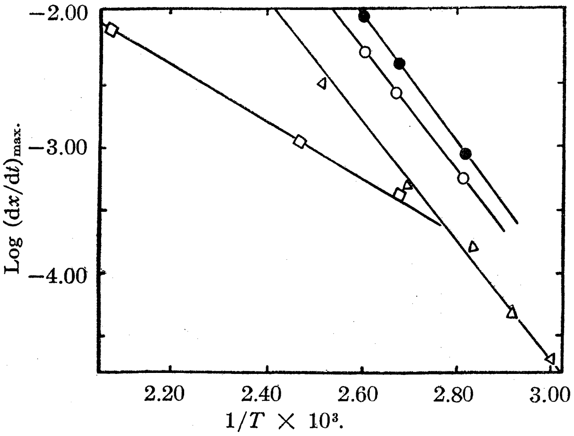

Fig. 3.—Decadic logarithm of maximum rate *vs.* the reciprocal of the absolute temperature: ○, 60% vinyl acetate in toluene; ●, undiluted vinyl acetate; △, styrene; □, methyl methacrylate (see Table I).

The average kinetic chain length, or "ν chain length," is equal to the ratio of the rate of (2) to the rate of (4), *i. e.*

$$\nu = k_2n/k_4N \qquad (17)$$

Since according to (6) the rate of polymerization is proportional to N, ν is inversely proportional to the rate. Although $k_2/k_4(=1/r)$ can be estimated from the course of the polymerization, the absolute value of N cannot be determined from such data, and so ν also evades evaluation.

The average "λ chain length" is equal to the ratio of the rate of (2) to the rate of (3). It follows that

$$\lambda = (k_2/k_3)f \qquad (18)$$

where f is a function of n (and perhaps of the amount of solvent also; *cf. seq.*) depending on the kinetic orders of (2) and (3). Reaction (2) is obviously second order, but the kinetic order of (3), which will be discussed in a later section, is uncertain. Whatever is the exact mechanism of (3), at the same concentration of monomer λ should be proportional to k_2/k_3 according to (18). If no chain branching (*cf. seq.*) occurs, λ is equal to the average degree of polymerization $D.\ P.$ Upon introducing the Arrhenius equation into the above proportionality relation

$$\log_{10}\lambda = \log_{10}(D.\ P.) = C + (E_3 - E_2)/2.303RT \quad (19)$$

where C is a constant.

In Table II the available data on the *D. P.*'s of polymers prepared at two or more temperatures are given. These are all based on estimates of molecular weights obtained by the Staudinger viscosity method.[23] In Fig. 4 the log (*D. P.*) values (Table II) for styrene, vinyl acetate and methyl methacrylate are shown to be linear functions of $1/T$ in agreement with (19). This simple quantitative relation of observed molecular weights to temperature stands in excellent confirmation of the theory developed above. The $E_3 - E_2$ values in the last column of the table have been calculated from the slopes of the lines in the figure; in the case of ethyl acrylate, where data are available at two temperatures only, $E_3 - E_2$ values have been calculated directly from equation (19).

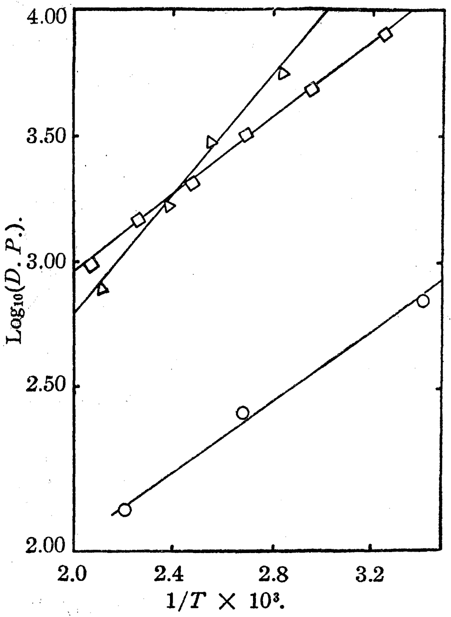

Fig. 4.—Log_{10} (*D. P.*) *vs.* $1/T$: ○, vinyl acetate; △, styrene; □, methyl methacrylate (see Table II).

TABLE II

DEGREE OF POLYMERIZATION AND $E_3 - E_2$

Substance	$T.$, °C.	$D.\ P.$[a]	Log_{10} $(D.\ P.)$	$1/T \times 10^3$ $(T.,\ °\text{K.})$	$E_3 -$ E_2, kcal.
Styrene[b]	80	5880	3.769	2.833	
Styrene[b]	100	4130	3.616	2.671	
Styrene[b]	120	2900	3.463	2.545	5.4
Styrene[b]	150	1710	3.233	2.364	
Styrene[b]	200	827	2.917	2.114	
Vinyl acetate[c]	20[f]	700	2.85	3.413	
Vinyl acetate[c]	100	250	2.40	2.681	3.2
Vinyl acetate[c]	180	100	2.00	2.208	
Methyl methacrylate[d]	35[f]	8000	3.906	3.247	
Methyl methacrylate[d]	65	4750	3.677	2.959	
Methyl methacrylate[d]	100	3210	3.513	2.681	
Methyl methacrylate[d]	132	2020	3.305	2.469	3.5
Methyl methacrylate[d]	170	1480	3.170	2.257	
Methyl methacrylate[d]	210	980	2.991	2.070	
Ethyl acrylate[e], 1 *M* in	100	78	1.892	2.681	4.8
butyl acetate	190	22	1.342	2.160	
Ethyl acrylate[e], 2 *M* in	100	145	2.161	2.681	4.5
butyl acetate	200	40	1.602	2.114	

[a] These are relative values of *D. P.*, which may only roughly approximate the correct absolute values. [b] Staudinger and Husemann, *Ber.*, **68**, 1618 (1935). [c] Staudinger and Schwalbach.[15] [d] Starkweather, Flory and Carothers.[20] [e] Staudinger and Trommsdorff.[34] [f] The 20° vinyl acetate polymer and 35° methyl methacrylate polymer were obtained by photopolymerizations.

Photochemical Polymerization.—The experiments of Taylor and Vernon[24] on the photopolymerizations of styrene and vinyl acetate are of particular interest because of their bearing on activation energies. Radiation in the near ultraviolet region (3000 to 4000 Å.), such as Taylor and Vernon used, is absorbed by the double bond and not by other parts of the molecule. Consequently, the initial step consists of activation of the monomer at the double bond, and not formation of free radicals through the dissociation of C–C or C–H bonds. Although many of the optically excited monomers must lose their energy in collisions with other molecules, some of them evidently react with other unexcited monomers yielding active centers and thereby initiating polymerization chains. Since the initiation of chains must therefore be second (or third) order[25] and since it may be assumed that other processes occurring in the polymerization are unaffected by the light, the theory given above for thermal poly-

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(23) Staudinger and Schulz, *Ber.*, **68**, 2320 (1935) have shown that for polystyrene the constant, K_m, in the Staudinger equation, $(\eta_r - 1)/C = K_m$ (M. W.), (η_r = relative viscosity of a dilute solution of polymer of concentration C) varies slightly with the temperature of polymerization, *e. g.*, from 0.61×10^{-4} at 80° to 0.41×10^{-4} at 200°. This behavior of polystyrene they attribute to chain branching (*cf. seq.*). Since it is the length of the chain (λ), rather than *D. P.*, which is primarily important in the evaluation of $E_3 - E_2$, and since according to Staudinger the viscosity molecular weight is fundamentally a measure of chain length, a constant value of K_m ($= 0.50 \times 10^{-4}$) has been preferred in calculating the *D. P.*'s for polystyrene in Table II from the $(\eta_r - 1)/C$ values given by Staudinger and Husemann. For the evaluation of $E_3 - E_2$, only relative values of M. W. at the various temperatures are required; hence, the absolute value of K_m is unimportant.

(24) H. S. Taylor and Vernon, THIS JOURNAL, **53**, 2527 (1931).

(25) In cases where all, or nearly all, of the incident light is absorbed, (1) may be first order because the amount of light absorbed is no longer dependent upon concentration.

merizations is equally applicable to photopolymerizations. Only the kinetic mechanism of reaction (1) differs in the two cases; E_a in equation (15) should be replaced by

$$E'_a = 1/2\, E'_1 + E_2 - 1/2\, E_4 \qquad (16.1)$$

where E'_1 is the activation energy which is required in addition to the photochemical excitation energy for the initiation of chains. E'_1 must be very small and within the limits of accuracy of the other E's, $1/2\, E'_1$ can be omitted in (16.1), *i. e.*

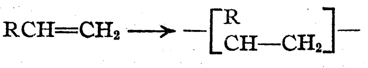
$$E'_a = E_2 - 1/2\, E_4 \qquad (16.2)$$

Taylor and Vernon found average 10° temperature coefficients of 1.30 for styrene in the range 30 to 100°, and 1.26 for vinyl acetate in the range 40 to 70°. For both substances the amount of light absorbed was independent of the temperature. The corresponding activation energies, E'_a, are 5.9 kcal. for styrene and 4.9 kcal. for vinyl acetate.

Activation Energies of Individual Reactions.—Combining the E'_a with the E_a values (equation 16) for these two compounds one obtains values for E_1, namely, 32 kcal. for styrene, and 35 kcal. for vinyl acetate. Assuming any reasonable value of $E_2 - 1/2\, E_4$ for methyl methacrylate, E_1 must be less than about 20 kcal., *i. e.*, appreciably less than for styrene or vinyl acetate. If, as mentioned before, the polymerization of methyl methacrylate was catalytic, a low value for E_1 is in accord with expectation. E_4, the energy requirement for the inter-reaction of two free radicals (whether it be by combination or disproportionation, *cf. seq.*) must be very low, certainly less than 5 kcal. Hence, from the values of $E'_a = E_2 - 1/2\, E_4$, E_2 must be about 6 kcal. for styrene and about 5 kcal. for vinyl acetate.[26,27] Recalling the values of $E_3 - E_2$ in Table II, E_3 for styrene must be about 12 kcal. and for vinyl acetate about 9 kcal.

Heats of Polymerization

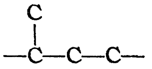
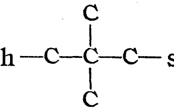
In a vinyl polymerization an unsaturated monomer is converted to a saturated (or less unsaturated) structural unit of a polymer molecule; that is



$$\mathrm{RCH{=}CH_2} \longrightarrow -\left[\begin{matrix}\mathrm{R} & \\ \mathrm{CH} & -\mathrm{CH_2}\end{matrix}\right]- \qquad (20)$$

Rossini[28] has shown that the heat of formation in kcal. of a straight chain paraffin hydrocarbon in the gaseous state is given by the linear function of n

$$\Delta H^\circ_{298} = -7.91 - 5.55n$$

when n, the number of carbon atoms, is greater than four. When $n < 5$, the following corrections must be applied to this equation: −1.59 kcal. for $n = 2$, −0.83 kcal. for $n = 3$, and −0.46 kcal. for $n = 4$. Rossini's[29] comparisons of heats of combustion of isobutane and tetramethylmethane with the heats of combustion of their respective straight chain isomers suggest that the above formula may be used for branched chain hydrocarbons by applying the corrections, −1.63 kcal. for each  $\overset{\mathrm{C}}{\underset{}{|}}$—C—C—C— structure and −4.9 (±1) kcal. for each  —C—$\underset{\mathrm{C}}{\overset{\mathrm{C}}{\mathrm{C}}}$—C— structure. With the aid of these corrections the heat of formation of any paraffin hydrocarbon can be calculated. The heat of formation of a structural unit of the polymer is

$$\Delta H_u = -5.55n + \Delta_u$$

where Δ_u is the sum of the corrections for each unit.

The very accurate determinations of heats of hydrogenation carried out by Kistiakowsky and co-workers[30] enable one to calculate the heats of formation of unsaturated hydrocarbons (monomer in (20)) using the formula

$$\Delta H_m = -7.91 - 5.55n - \Delta H_{hyd} + \Delta_m$$

where ΔH_m is the heat of formation of the gaseous unsaturated monomer, ΔH_{hyd} is the heat of hydrogenation to the corresponding saturated hydrocarbon, and Δ_m is the sum of the corrections for this saturated hydrocarbon. The heat of polymerization is then

$$\Delta H_p = \Delta H_u - \Delta H_m = 7.91 + \Delta H_{hyd} + \Delta_u - \Delta_m \quad (21)$$

The very small correction necessary for conversion of ΔH_p to the liquid state will be overlooked. If the monomer is a diolefin (*e. g.*, if R in (20) is unsaturated), ΔH_{hyd} is the heat of hydrogenation of both double bonds and allowance must be made in Δ_u for the heat of hydrogenation of the single unsaturated group in the polymer unit (29.95 kcal. for $-\mathrm{CH{=}CH_2}$ and 27.80 kcal. for $-\mathrm{CH{=}CH}-$).

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[26] Melville, *Trans. Faraday Soc.*, **32**, 258 (1936), has estimated that E_2 in the polymerization of gaseous acetylene is about 4 kcal.

[27] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, p. 190, state that the addition of ethylene to an alkyl free radical probably requires less than 10 kcal. of activation energy.

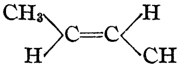
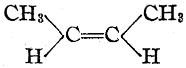
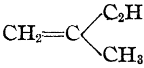
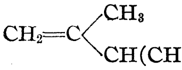
[28] Rossini, *Bur. Standards J. Research*, **13**, 21 (1934).

[29] Rossini, *J. Chem. Phys.*, **3**, 438 (1935).

[30] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935); Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935); **58**, 137 (1936); **58**, 146 (1936).

Heats of polymerization calculated from the data of Rossini and of Kistiakowsky and co-workers using equation (21) are given in Table III.

TABLE III
HEATS OF POLYMERIZATION

Monomer	$\Delta H_{\text{hyd}}{}^{a}$ (298°K.)	Δ_u	Δ_m	ΔH_p (298°K.)
C_2H_4	−32.57	0	−1.59	−23.07
C_3H_6	−29.86	−1.63	−0.83	−22.75
$C_2H_5—CH=CH_2$	−30.09	−1.63	−0.46	−23.35
	−27.37	−3.26	−0.46	−22.26
	−28.32	−3.26	−0.46	−23.21
$C_2H_5—CH=CH—CH_3$ (*cis* + *trans*)	−27.70	−3.26	0	−23.05
$C_5H_{11}—CH=CH_2$	−29.89	−1.63	0	−23.61
$CH_2=C(CH_3)_2$	−28.14	−4.9	−2.1	−23.0
	−28.24	−4.9	−1.63	−23.6
	−27.75	−6.5	−3.26	−23.1
$CH_2=CH—CH=CH_2$ (1,2-polymerization)	−56.57	28.32	−0.46	−19.88
$CH_2=CH—CH=CH_2$ (1,4-polymerization)	−56.57	27.80	−0.46	−20.40
$CH_2=CH—CH_2—CH=CH_2$ (1,2-polymerization)	−60.29	28.32	0	−24.06

[a] Kistiakowsky and co-workers give heats of hydrogenation at 355°K. These have been corrected to 298°K. by assuming that the correction for all olefins is the same as for ethylene, namely, +0.25 kcal. For diolefins 0.50 kcal. has been used.

It is significant that for all of the mono-olefins the heat of polymerization approximates −23.0 kcal. in spite of the wide variations in structure. For conjugated diolefins ΔH_p is about 20 kcal. For styrene there are no direct thermochemical data upon which to base a value of ΔH_p. However, Kharasch[31] in his calculations of heats of combustion from the principle of bond additivity uses a correction of −3.5 kcal. for an aryl-alkyl linkage and −6.5 kcal. for an aryl-vinyl linkage. It follows that the heat of polymerization of styrene should be about 3 kcal. less than the "normal" value of 23 kcal., which leads to a value the same as for conjugated diolefins.

Reaction Mechanisms

Chain Initiation.—The only conceivable unimolecular processes by which (1) might occur are the formation of free radicals through the spontaneous dissociation of a C–C or a C–H bond, or the opening of the double bond to yield a divalent free radical. The value for D_{C-C}, the heat of dissociation of a carbon-carbon bond, is about 75 kcal.[32] and D_{C-H} is about 95 kcal., although these values may be somewhat affected by substituent groups.[33] The opening of a double bond should require about 60 kcal. The much smaller experimental values for E_1 definitely rule out these unimolecular mechanisms of chain initiation.

A second order mechanism such as

$$2CH_2=CHR \longrightarrow CH_3—CHR— + CH_2=CR— \quad (1.1)$$

in which two free radicals are formed by the exchange of a hydrogen atom, also requires too much energy.

For the process in which two monomers are coupled to form a di-free radical, *viz.*

$$2CH_2=CHR \longrightarrow —CHR—CH_2—CH_2—CHR— \quad (1.2)$$

$\Delta H_{1\cdot 2} = D_{C-C} + 2\Delta H_p$; $\Delta H_{1\cdot 2} = 29$ kcal., when $R = H$. When the monomer is a substituted ethylene (*e. g.*, when $R = H$), $\Delta H_{1\cdot 2}$ will be lowered due to the effect of substituents in stabilizing free radical groups; *i. e.*, as Conant[33] has pointed out, D_{C-C} is lowered by the substituents on the carbon atoms separated on dissociation. Consequently, for styrene and vinyl acetate the estimate for $\Delta H_{1\cdot 2}$ should be less than the above value of 29 kcal., and compliance of this mechanism with the necessary condition, $\Delta H_1 < E_1$ (see above experimental values for E_1), is thus assured.

Although the above mechanism (1.2) appears quite plausible, it is open to the objection that reversal of (1.2) might occur with such ease that it should be written as an equilibrium. If this be the case the initiation of chains becomes third order, *viz.*

$$2CH_2=CHR \rightleftarrows —CHR—CH_2—CH_2—CHR— + CH_2=CHR \longrightarrow —CHR—CH_2—CHR—CH_2—CH_2—CHR— \quad (1.3)$$

E_1 according to this mechanism will be the sum of the heat of the first reaction and the activation of the second step. Since this second step is equivalent to (2), $E_{1\cdot 3} = \Delta H_{1\cdot 2} + E_2$. If $R = H$, $E_{1\cdot 3} \cong 35$ kcal.; if $R \neq H$, $E_{1\cdot 3}$ should be some-

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(31) Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929).

(32) As yet no reliable value has been obtained for the strength of a C–C or a C–H bond in an ordinary hydrocarbon. Rossini's[28] heats of formation of hydrocarbons and Schmid's [*Z. Physik*, **99**, 274, 281 (1936)] recent work on the heat of dissociation of CO can be combined to yield the heats of *complete* dissociation of hydrocarbons, but not to yield the heat of dissociation of a single bond without rupture of the other bonds in the molecule. The above values of D_{C-C} have been chosen largely on the basis of the activation energies for dissociation of ethane and propane into free radicals, given by Rice and Rice[27] (book, p. 78).

(33) Conant, *J. Chem. Phys.*, **1**, 427 (1933), has suggested that the reduction of D_{C-C} by substituents on the carbons joined by the bond dissociated is approximately an additive effect, D_{C-C} being lowered 6 kcal. by each alkyl group and 11 kcal. by each aryl group.

what less than this. These values are also in agreement with the experimental values of E_1, and choice between these similar mechanisms, (1.2) and (1.3), is impossible at present. For this reason two theoretical treatments, one for second order and one for third order chain initiation, have been presented above.

In either mechanism (1.2) or (1.3) the dimeric free radical having the substituted groups at its ends is the most likely to form since, according to Conant's conclusions, this is the most stable structure. The presence of substituents, especially negative substituents such as C_6H_5— and CH_3-OCO— on one of the carbons adjoining the double bond of the monomer should render the dimeric intermediate more stable[33] and consequently lower E_1 and facilitate the polymerization. This conclusion is in agreement with fact as shown by the tabulations of Staudinger (Tables I and II of reference 5); *e. g.*, $CH_2{=}C(CH_3)_2$ polymerizes more readily than either $CH_2{=}CH_2$ or $CH_2{=}CH{-}CH_3$, and $CH_2{=}CH{-}C_6H_5$ more readily than $CH_2{=}CH{-}CH_3$. By the same argument the coupling reaction (2) should nearly always take place between the free radical and the unsubstituted (or less substituted) carbon of the vinyl group, so that the "new" free radical will appear at the substituted end of the vinyl group. This leads to the formation of a chain having a preponderance of the substituents *R* on alternate carbon atoms.

Chain Transfer.—In order to explain the approximate constancy of molecular weight during polymerization, Schulz[13] has concluded that the process which causes cessation of polymer growth is of the same kinetic order as polymer growth. In the light of the present concepts, this means that reaction (3) is of the same kinetic order as (2), *i. e.*, second order. On the other hand, there is an abundance of evidence to show that the molecular weight of the polymer decreases on dilution of the monomer with an inert solvent. For example, Staudinger and Schwalbach[15] by polymerizing a 50% solution of vinyl acetate in benzene obtained a polymer of roughly half the molecular weight of a polymer prepared from undiluted vinyl acetate at the same temperature. The molecular weights of the polyethyl acrylates prepared by Staudinger and Trommsdorff[34] from undiluted monomer and solutions of various concentrations of monomer in butyl acetate are approximately proportional to the concentration. These results indicate that (3) is of lower kinetic order than (2), *i. e.*, that (3) is first order, in disagreement with Schulz's conclusion and equation (18). Any unimolecular mechanism for the process of chain transfer would of necessity consist of the expulsion of a free radical, or a hydrogen atom, from the chain bearing the free bond with simultaneous formation of a double bond in the chain molecule; for example

$$\mathrm{M}_n{-}\mathrm{CH_2}{-}\mathrm{CHR}{-} \longrightarrow \mathrm{M}_n{-}\mathrm{CH}{=}\mathrm{CHR} + \mathrm{H} \qquad (3.1)$$

where M_n denotes a sequence of *n* structural units preceding the terminal structural unit of the polymer. ΔH for this process is about 35 or 40 kcal., and for the expulsion of an alkyl group ΔH $(= -\Delta H_p)$ is about 20 kcal. Both values are so much greater than E_3 estimated from experimental data (13 and 9 kcal., see above) that it is necessary to reject unimolecular mechanisms.

Taylor and Jones[6] have proposed the bimolecular chain transfer reaction

$$\mathrm{M}_n{-}\mathrm{CH_2}{-}\mathrm{CHR}{-} + \mathrm{CH_2}{=}\mathrm{CHR} \longrightarrow \mathrm{M}_n - \mathrm{CH_2}{=}\mathrm{CHR} + \mathrm{CH_3}{-}\mathrm{CHR}{-} \qquad (3.2)$$

in order to explain their results on the polymerization of gaseous ethylene. Another possible mechanism for (3) consists of saturation of the free radical with an atom from another molecule, for example

$$\mathrm{M}_n{-}\mathrm{CH_2}{-}\mathrm{CHR}{-} + \mathrm{R'}{-}\mathrm{CH_2}{-}\mathrm{R''} \longrightarrow \mathrm{M}_n{-}\mathrm{CH_2}{-}\mathrm{CH_2R} + \mathrm{R'}{-}\overset{|}{\mathrm{C}}\mathrm{H}{-}\mathrm{R''} \qquad (3.3)$$

The molecule R′—CH$_2$—R″ might be a monomer, a polymer or a solvent molecule. Rice and Rice[27] estimate that the activation energy for such a reaction is about 20 kcal. when the R's are alkyl groups and appreciably lower than this when either R′ or R″ is a negative group. Both of these bimolecular reactions (3.2) and (3.3) lead to constancy of molecular weight during polymerization. Participation of the solvent in (3.3) would provide an explanation of the decrease in molecular weight upon dilution with solvent. Choice of a definite mechanism for (3) is not possible at present, however.

Chain Termination.—The destruction of active centers by the inter-reaction of two of them may involve the coupling of the two radicals

$$\mathrm{M}_m{-}\mathrm{CH_2}{-}\mathrm{CHR}{-} + \mathrm{M}_n{-}\mathrm{CH_2}{-}\mathrm{CHR}{-} \longrightarrow \mathrm{M}_m{-}\mathrm{CH_2}{-}\mathrm{CHR}{-}\mathrm{CHR}{-}\mathrm{CH_2}{-}\mathrm{M}_n \qquad (4.1)$$

or the disproportionation reaction

$$\mathrm{M}_m{-}\mathrm{CH_2}{-}\mathrm{CHR}{-} + \mathrm{M}_n{-}\mathrm{CH_2}{-}\mathrm{CHR}{-} \longrightarrow \mathrm{M}_m{-}\mathrm{CH_2}{-}\mathrm{CH_2R} + \mathrm{M}_n{-}\mathrm{CH}{=}\mathrm{CHR} \qquad (4.2)$$

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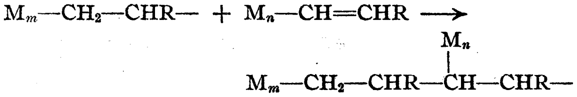
(34) Staudinger and Trommsdorff, *Ann.*, **502**, 201 (1933).

Neither of these reactions should require a preactivation energy. Cramer[35] has concluded that in the recombination of ethyl radicals in benzene solution disproportionation (4.2) predominates over coupling (4.1).

Chain Branching and Molecular Weights.—That each polymer molecule has on the average one double bond has been shown by Staudinger and Steinhofer[36] for catalytically polymerized polystyrene, and by Whitby,[37] for polyindene. In both instances this observation has been advanced in an effort to prove particular mechanisms for the polymerization processes. Regardless of the mechanism of the polymerization, if extraneous substances (including solvents) are either completely absent or do not participate in the polymerization, and if no cyclic structures or triple bonds are formed, the polymerization of a monovinyl compound must yield a mixture of molecules having an average of one double bond each. Consequently, the formation of unsaturated polymer molecules in vinyl polymerizations is inevitable and not an indication of the mechanism involved.

Theoretically, a polymer molecule bearing a double bond is susceptible to reaction with a free radical according to (2), and thus a polymer molecule may be included as one member of a polymerization chain; thus, for example



$$\mathrm{M}_m\text{—CH}_2\text{—CHR— } + \mathrm{M}_n\text{—CH=CHR} \longrightarrow \mathrm{M}_m\text{—CH}_2\text{—CHR—}\overset{\mathrm{M}_n}{\overset{|}{\text{CH}}}\text{—CHR—}$$

The frequency of the formation of branched chain molecules in this way must depend upon the relative reactivities with respect to (2) of the double bonds in polymers and those in monomers, and upon the relative numbers of polymers and monomers. If chain transfer proceeds according to (3.3), occasionally a free radical active center may be transferred to some point along the chain of a previously formed polymer molecule; subsequent growth from this center would also yield a branched chain. The possibility that inactive polymer molecules may participate in the subsequent polymerization is implied by both chain branching mechanisms. Houtz and Adkins[38] have presented experimental evidence to show that polystyrene added to polymerizing monomer actually does undergo further polymerization. The results of Staudinger and Frost[4] on the relative viscosities of solutions of polystyrene obtained at various stages of the polymerization show a slight increase as the reaction progresses, which may be an indication of an increase in molecular weight due to participation of "inactive" polymer in the subsequent polymerization. Staudinger and Schulz[23] have observed that a series of polystyrenes prepared at different temperatures deviate from strict adherence to the Staudinger viscosity law. They attribute this deviation to a particular type of chain branching reaction involving the disruption of the hexatriene bond structure of the phenyl group. Such a reaction would require a great deal of energy, and in the absence of definite evidence it seems preferable to avoid a specific mechanism in favor of the general explanation of chain branching given above.[39]

During the early stages of the polymerization when the quantity of monomer exceeds the quantity of polymer, branched chain molecules must be few. The average degree of polymerization should not differ appreciably from λ and the distribution of molecular sizes derived by Schulz[13,40] should prevail. At later stages of the polymerization the occurrence of chain branching may become appreciable. If so, *D. P.* will exceed λ and the distribution of molecular sizes will deviate from Schulz's distribution theory. If, as Staudinger claims, the viscosity of a dilute solution of polymer depends upon the length of the molecule and is independent of its lateral dimensions, the apparent viscosity molecular weight should no longer be proportional to *D. P.*

Since this article was submitted Schulz and Husemann[41] have published a comprehensive paper on the kinetics of styrene polymerization. Their basic concepts of the polymerization mechanism, the same as previously published by Staudinger and Frost[4] and by Schulz,[13] differ principally from those presented in this paper in that they do not include reaction (3). The kinetics of the conversion of monomer to polymer, which depends only upon (1), (2) and (4), should be essentially the same regardless of which interpretation is adopted. However, the equations given above

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(35) Cramer, This Journal, **56**, 1234 (1934).

(36) Staudinger and Steinhofer, *Ann.*, **517**, 35 (1935).

(37) Whitby, *Trans. Faraday Soc.*, **32**, 315 (1936).

(38) Houtz and Adkins, This Journal, **55**, 1609 (1933).

(39) From measurements of streaming double refraction, Signer [*Helv. Chim. Acta*, **19**, 897 (1936)] has shown recently that Staudinger and Schulz's polystyrenes prepared at higher temperatures consist of molecules less nearly linear in shape than those prepared at lower temperatures.

(40) This distribution is identical with that obtained by the author [*ibid.*, **58**, 1877 (1936)] for linear condensation polymers, although the equations differ slightly in their form.

(41) Schulz and Husemann, *Z. physik. Chem.*, **B34**, 187–213 (1936).

differ a great deal from those given by Schulz and Husemann. The source of the dissimilarity lies in the different expressions obtained for the concentration of active centers, namely, equation (7) in this paper and their equation (12). The latter is incorrect for chain reactions in which the active centers are simultaneously created and destroyed.

From their experimental measurements they have derived 23.2 kcal. for the quantity herein designated as E_a. From the same data as quoted here, they obtain 5.7 kcal. for "Q," which according to the method of evaluation is equivalent to $E_3 - E_2$. These values are in good agreement with the ones given above. The present interpretation of these quantities is much different, however; *e. g.*, Schulz and Husemann regard E_a as equal to the activation energy of (1). Consistent interpretation according to the mechanism which they assume leads to $Q = 5.7$ kcal. $= E_4 - E_2$. That the activation energy E_4 for the reaction of two free radicals with one another should exceed the activation energy E_2 for the reaction of a free radical with a monomer molecule seems exceedingly unlikely.

The author is particularly indebted to Drs. Wallace H. Carothers and Elmer O. Kraemer for their valuable criticisms of this work.

Summary

A mechanism consisting of the four processes, (1) chain initiation, (2) chain propagation, (3) chain transfer and (4) destruction of active centers, has been proposed to account for the known characteristics of typical vinyl polymerizations. The free radical active centers must of necessity be both created (1) and destroyed (4) in pairs. The previously proposed process of coupling of monomers to the free radical through the opening of the double bond has been adopted for chain propagation (2). A chain transfer process (3), whereby the active center is transferred from one polymer molecule to another molecule, leaving the former "inactive" and endowing the latter with the ability to add on monomers successively (2), has been introduced in order to account for the independence of molecular weight on number of active centers.

Upon the basis of this mechanism, the kinetics of the conversion of monomer to polymer has been subjected to a theoretical analysis and equations have been derived to represent the course of the conversion. These are in satisfactory agreement with the limited available experimental data. The variation of relative molecular weight with temperature is in excellent agreement with the proposed mechanism for vinyl polymerizations.

Activation energies of the individual processes have been estimated from experimental data; the approximate values are: for styrene $E_1 = 32$ kcal., $E_2 = 6$ kcal., and $E_3 = 12$ kcal.; for vinyl acetate, $E_1 = 35$ kcal., $E_2 = 5$ kcal. and $E_3 = 9$ kcal.; for methyl methacrylate $E_1 < 20$ kcal. It has been assumed that $E_4 < 5$ kcal. in consideration of the ease with which two free radicals should inter-react. Heats of polymerization, ΔH_p, have been calculated for a number of unsaturated compounds from the recent thermochemical data of Rossini and Kistiakowsky and co-workers. For all types of mono-olefins $\Delta H_p = -23\ (\pm 1)$ kcal.; for conjugated diolefins (styrene included) $\Delta H_p = 20$ kcal.

In the light of their activation energies probable mechanisms for the individual reactions have been presented. The occasional formation of branched chain molecules is theoretically probable.

WILMINGTON, DEL. RECEIVED OCTOBER 26, 1936

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

Ammonia. The Heat Capacity and Vapor Pressure of Solid and Liquid. Heat of Vaporization. The Entropy Values from Thermal and Spectroscopic Data

BY ROY OVERSTREET AND W. F. GIAUQUE

In a former communication, Giauque, Blue and Overstreet[1] showed that the existing low temperature calorimetric data on ammonia lead to an entropy value about one cal./deg. per mole greater than the value obtained from band spectrum observations. The purpose of this research has been to obtain accurate calorimetric data in the hope of eliminating the discrepancy. As was expected, the inconsistency was found to be due chiefly to the inaccuracy of the existing calorimetric data.

Preparation of Ammonia.—The ammonia used in this investigation was prepared by the action of a saturated solution of potassium hydroxide on C. P. ammonium chloride. The gas was subjected to a preliminary drying by conducting it slowly through a vertical glass column, approximately one meter in length, containing broken sticks of potassium hydroxide. The ammonia issuing from the column was condensed over sodium in one of a series of glass distillation bulbs by means of solid carbon dioxide in ether. Approximately 250 cc. of liquid was prepared in this manner. After standing over sodium for twelve hours, the substance was then distilled five times. In each case the first 10 cc. of distillate and the final 10 cc. portion was discarded. Following each distillation, the gas was cooled to the temperature of liquid air and the line was evacuated to 10^{-5} mm.

The amount of liquid-soluble solid-insoluble impurity was estimated to be not more than one mole in one hundred thousand. This estimate was made on the assumption that the slight rise in heat capacity below the melting point was due to premelting. The single high observation given later in Table IV was confirmed by several measurements, not included, over smaller temperature intervals just below the melting point.

Apparatus.—The measurements were carried out in Gold Calorimeter II[2] which was rebuilt and described by Blue and Giauque.[3] A full description of a calorimeter of this type has been given by Giauque and Egan.[4]

The temperature scale was obtained from the copper-constantan thermocouple of laboratory designation "W."[5] The thermocouple, which was originally compared with a hydrogen gas thermometer, has been compared frequently with the oxygen and hydrogen vapor pressure thermometers. The latest comparison, made after the completion of this work, gave the following corrections to be added to the original calibration made nine years before: 0.01° at the boiling point of oxygen, 90.13° K., 0.11° at the melting point of oxygen, 54.39° K., 0.13° at the 43.76° K. transition of oxygen, 0.15° at the boiling point of hydrogen 20.37° K. and 0.17° at the triple point of hydrogen, 13.95° K. These corrections were employed in the temperature scale used in this research. The gold resistance thermometer-heater, used for greater calorimetric precision and accuracy, was calibrated continuously during the measurements by comparison with the thermocouple.

The Vapor Pressure of Ammonia.—The vapor pressure was determined by means of a manometer which could be connected directly with the calorimeter. A cathetometer was used as a comparison instrument with a standard meter mounted in the manometer case. The vapor pressure observations on solid ammonia from 176.92°K. to the melting point, 195.36°K., have been represented by the equation

$$\log_{10} P \text{ (int. cm. Hg)} = -1630.700/T + 9.00593 \quad (1)$$

For liquid ammonia from 199.26 to 241.59°K.

$$\log_{10} P \text{ (int. cm. Hg)} = -1612.500/T - 0.012311\ T + 0.0000125217T^2 + 10.83997 \quad (2)$$

In Table I the observed values are compared with those given by equations 1 and 2. The pressure observations are corrected to international centimeters of mercury by means of data given in the "I.C.T."[6] The standard acceleration of gravity was taken as 980.665 cm./sec.². The gravitational acceleration, 979.973 cm./sec.² has been determined for this location by Sternewarte.[7] Because of the high relative accuracy, which could be obtained with the resistance thermometer, the temperatures for the liquid are given to 0.001°. The absolute error may be as high as several hundredths of a degree.

From equation 2 the boiling point was calculated to be 239.68°K.

The deviations given in the third column of Table I were calculated by assuming that the temperature observations were correct. The deviations given in the fourth column of the table were calculated assuming that the pressures were correct.

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[1] Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

[2] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

[3] Blue and Giauque, *ibid.*, **57**, 991 (1935).

[4] Giauque and Egan, *J. Chem. Phys.*, in press.

[5] (a) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

[6] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. I, 1926.

[7] Sternewarte, Landolt, Börnstein and Roth, "Physikalische chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

TABLE I

VAPOR PRESSURE OF AMMONIA

Boiling point 239.68°K. 0°C. = 273.10°K.

T, °K.	P, obsd., int. cm. Hg.	P, obsd. − P, calcd.	T, measd. − T, calcd.	
176.92	0.615	0.000	0.00	Solid
181.13	1.010	.003	−.03	Solid
183.17	1.266	−.002	.02	Solid
186.00	1.735	.002	−.01	Solid
189.03	2.398	.003	−.01	Solid
191.85	3.206	−.001	.00	Solid
195.360	4.558	.000	.000	Triple point
199.262	6.188	−.001	.003	Liquid
203.114	8.261	−.001	.002	Liquid
206.587	10.608	.000	.000	Liquid
210.811	14.181	−.003	.001	Liquid
214.420	18.017	.003	−.002	Liquid
218.354	23.126	.006	−.004	Liquid
224.246	32.980	.008	−.004	Liquid
229.205	43.725	−.010	.004	Liquid
234.840	59.284	−.009	.003	Liquid
241.585	83.535	−.010	.002	Liquid

A summary of observations on the melting point temperature is given in Table II. Observation 1 was a single determination. Observations 2 and 3 were taken consecutively over a period of about two hours. Observations 4, 5 and 6 were taken consecutively over a period of approximately five hours. Table III contains a summary of the more recent determinations of the melting and boiling points of ammonia.

TABLE II

MELTING POINT OF AMMONIA

0°C. = 273.10°K.

Observation	% melted	T, °K. Resistance thermometer	T, °K. Thermocouple	P, int. cm. Hg
1	20	195.350	195.36	4.557
2	15	195.355	195.36	4.559
3	25	195.358	195.37	4.557
4	5	195.360	195.35	4.560
5	15	195.361	195.35	4.558
6	30	195.364	195.36	4.559
		Accepted values	195.36	4.558

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF AMMONIA

M. p., °K.	B. p., °K.	Observer
....	239.90	Keyes and Brownlee[8] (1918)
195.40	239.75	Cragoe, Meyers and Taylor[9] (1920)
....	239.74	Henning and Stock[10] (1921)
195.5	....	Eucken and Karwat[11] (1924)
195.36	239.68	This research

As may be seen from Table III the melting and boiling point temperatures agree fairly well with those obtained by Cragoe, Meyers and Taylor[9] and by Henning and Stock.[10] The latter authors did not make observations at the melting point but by substituting the observed triple point pressure in their vapor pressure equation the value 195.39°K. is found as compared to the present observation of 195.36°K.

The present value obtained for the boiling point is 0.07° below that of Cragoe, Meyers and Taylor and 0.06° below that of Henning and Stock.

The agreement is perhaps all that can be expected when one considers the possible errors of the several experimenters. The gas thermometer scale calibration by Giauque, Buffington and Schulze,[5a] of the thermocouple used in the present work, was estimated by those authors to be accurate to ±0.05°. However, high relative accuracy was obtained by means of the resistance thermometer which was read with a scale giving about 10^4 mm. per degree. The resistance thermometer was calibrated by comparison with the thermocouple at frequent intervals over a wide temperature range.

The value, 4.558 cm., given for the triple point pressure is in good agreement with an observation of Bergstrom[11a] who obtained 4.55 cm. Also by putting the melting point observation of the present research in the vapor pressure equation of Henning and Stock one obtains the value 4.55 cm. The observation, 4.49 cm., of Cragoe, Meyers and Taylor is evidently in error. Putting their value for the melting point, 195.40°K., into their vapor pressure equation one obtains 4.53 cm.

The Heat Capacity of Ammonia.—The heat capacity results are given in Table IV. For the calculation of energy, 1.0004 absolute joules were taken equal to 1 international joule and 4.185 absolute joules were taken equal to 1 calorie. The data are shown in Fig. 1. The heat capacity of ammonia has been measured by Eucken and Karwat[11] and by Clusius, Hiller and Vaughen.[12] In Table V are recorded heat capacity values picked from a smooth curve through the observations. Since Eucken and Karwat have prepared a similar table, deviations from their data are included. Deviations from the data of Clusius, Hiller and Vaughen are not included, since their investigations were carried out, for the most part, at temperatures below 20°K. However, their data at higher temperatures are too high by

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[8] Keyes and Brownlee, THIS JOURNAL, **40**, 25 (1918).

[9] Cragoe, Meyers and Taylor, *ibid.*, **42**, 206 (1920).

[10] Henning and Stock, *Z. Physik*, **4**, 226 (1921).

[11] Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924).

[11a] Bergstrom, *J. Phys. Chem.*, **26**, 358 (1922).

[12] Clusius, Hiller and Vaughen, *Z. physik. Chem.*, **B8**, 427 (1930).

approximately the same percentages as those given for Eucken and Karwat in Table V.

TABLE IV

HEAT CAPACITY OF AMMONIA

Molecular weight 17.031; 0°C. = 273.10°K.

Series I, II, III and IV 4.3558 moles. Series V 4.3321 moles.

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
15.04	0.780	0.176	130.87	5.038	8.152
15.71	1.097	.200	135.80	4.726	8.484
17.26	1.714	.237	140.47	4.502	8.714
19.75	2.960	.358	145.32	4.987	8.972
22.74	3.007	.529	150.23	4.673	9.304
26.08	3.588	.750	155.35	5.073	9.594
29.74	3.462	1.013	160.40	4.824	9.866
33.46	3.883	1.313	165.58	5.263	10.16
37.78	4.664	1.666	170.85	4.984	10.45
42.32	4.423	2.031	175.86	4.732	10.77
46.79	4.413	2.391	180.99	5.125	11.10
51.23	4.490	2.758	186.16	4.861	11.45
56.11	5.246	3.173	191.09	4.612	11.94
61.24	4.965	3.567	195.36	Melting point	
65.47	3.789	3.913	197.84	3.733	17.54
69.69	4.511	4.217	202.31	4.944	17.60
74.63	5.185	4.563	207.28	4.798	17.71
79.56	4.674	4.926	212.32	5.072	17.75
84.05	4.296	5.234	217.42	4.915	17.89
88.70	4.902	5.535	219.59	4.870	17.90
93.44	4.755	5.831	222.60	5.134	17.94
98.32	5.083	6.172	225.02	4.754	17.96
103.24	4.750	6.447	227.94	5.134	18.02
107.87	4.454	6.743	229.93	4.655	18.02
112.71	4.979	7.044	233.15	5.016	18.05
117.55	4.666	7.356	234.76	4.563	18.05
119.50	4.175	7.491	238.33	4.897	18.12
122.11	4.419	7.621	239.68	Boiling point	
125.97	4.565	7.858			

TABLE V

HEAT CAPACITY OF AMMONIA

Molecular weight 17.031, 0°C. = 273.10°K.

Values taken from smooth curve through observations

T, °K.	C_p	Deviation %. E. and K.— This research	T, °K.	C_p	Deviation %. E. and K.— This research
20	0.368	−4.4	140	8.699	4.7
30	1.033	0.8	150	9.272	4.6
40	1.841	8.9	160	9.846	4.3
50	2.663	13.6	170	10.42	3.8
60	3.474	10.2	180	11.03	3.2
70	4.232	7.6	190	11.71	2.0
80	4.954	6.0	200	17.58	4.6
90	5.612	5.4	210	17.75	2.9
100	6.246	5.3	220	17.90	1.5
110	6.877	5.1	230	18.03	0.7
120	7.497	4.8	240	18.12	0.5
130	8.102	4.8			

Heat of Fusion.—Determinations of the heat of fusion of ammonia are given in Table VI. With the temperature slightly below the melting point, heat was added until all of the substance was melted and the liquid heated slightly above the melting point. Correction was made for the $\int C_p dT$ and the premelting effect. It is interesting to compare the value for the heat of fusion obtained in this research with that calculated by Eucken and Donath[13] from measurements of the heat of sublimation and heat of vaporization near the melting point. By a small extrapolation of their heat of condensation measurements, they have calculated the difference between the heat of sublimation and the heat of vaporization at the melting point to be 1380 ± 8 cal. Considering the large quantities of heat dealt with, the agreement between their value and the value of this research is good.

TABLE VI

HEAT OF FUSION OF AMMONIA

Temperature interval	Corrected heat, input/mole	$\int C_p dT$	ΔH
193.688–196.684	1402.4	50.9	1351.5
193.638–195.919	1388.3	36.4	1351.9
193.416–196.539	1403.5	52.0	1351.5
		Mean	1351.6 ± 0.2
Eucken and Karwat[11]			1426
Eucken and Donath,[13] from heats of sublimation and heat of vaporization			1380 ± 8
From vapor pressure equations of this research, assuming a Berthelot gas			1376

Heat of Vaporization.—The heat of vaporization was measured by adding energy and determining the amount of gas evolved. The ammonia was vaporized against a constant pressure, which was slightly above atmospheric pressure. A small correction was applied to obtain the value corresponding to 760 mm. A summary of the data is given in Table VII. Osborne and Van Dusen[14] have measured the heat of vaporization of ammonia through the range −42 to +52°. The value 5573 interpolated from their data is in excellent agreement with the value obtained in this research.

It has been of interest to calculate the heat of fusion and the heat of vaporization from the vapor pressure data. This has been done by assuming that Berthelot's equation of state can be used to correct for gas imperfection. The values are included in Tables VI and VII. The agreement with the experimental values is sufficiently close to justify the use of Berthelot's equation for the calculation of the entropy correction for the actual to the ideal gas states.

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(13) Eucken and Donath, *Z. physik. Chem.*, **124**, 181 (1926).

(14) Osborne and Van Dusen, THIS JOURNAL, **40**, 14 (1918).

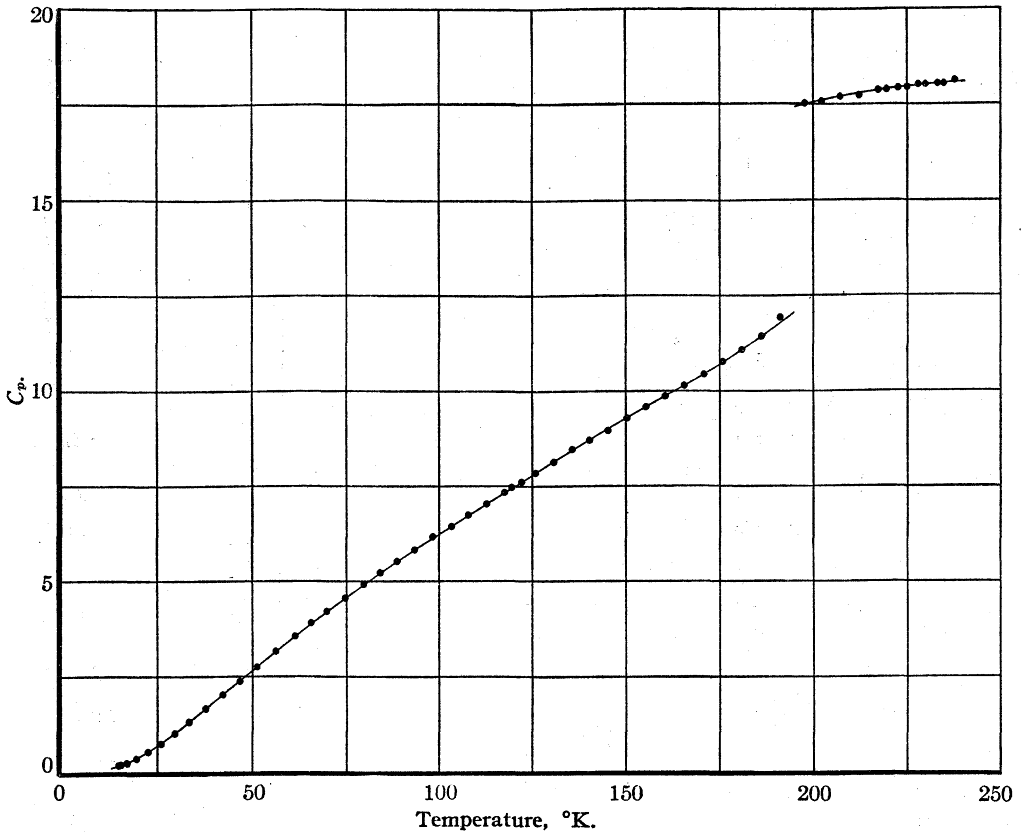

Fig. 1.—Heat capacity in calories per degree per mole of ammonia.

TABLE VII

HEAT OF VAPORIZATION OF AMMONIA

Boiling point 239.68°K. 0°C. = 273.10°K. Molecular weight 17.031

Amount evaporated, mole	Total of energy input, min.	ΔH at 760 mm. cal./mole
0.32400	100	5586
.39086	120	5590
.39197	120	5570
.36888	100	5581
.33913	100	5573
.38839	110	5589
.37590	100	5575
	Mean	5581
Osborne and Van Dusen		5573
From vapor pressure equation 2, assuming a Berthelot gas		5614

Measurement of Amount of Ammonia.—All amounts were measured gravimetrically. The gas vaporized during the heat of vaporization runs was absorbed in 6 N sulfuric acid and weighed. The absorption bulbs were of 110-cc. capacity. All necessary precautions were taken to avoid loss of moisture from the bulb to the outside or the gain of moisture in the bulb from the outside. Following the heat of vaporization runs, the remainder was absorbed in a large absorption bulb (800 cc.) containing 6 N sulfuric acid and weighed. The small amount of gas remaining in the apparatus was calculated from the pressure and volume.

The Entropy from Calorimetric Data.—The entropy was calculated by graphical integration of $\int_0^T C_p \, d \ln T$ plus the entropies of fusion and vaporization. The entropy correction for gas imperfection was made using Berthelot's equation of state and the thermodynamic equation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{from which}$$

$$\Delta S = S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c$$

$T_c = 406.0$°K.[15] and $P_c = 112.3$ atmospheres[15]

Then $\Delta S = 0.07$ e. u. at the boiling point of ammonia. The entropy calculation is summarized in Table VIII.

The Entropy of Ammonia from Spectroscopic Data.—The translational entropy of ammonia was obtained from the Sackur–Tetrode equation

$$S_T = 3/2R \ln M + 5/2\, R \ln T - R \ln P + 5/2\, R + R \ln (2\pi k)^{3/2}/h^3N^{5/2} + R \ln R \quad (3)$$

$$= 3/2R \ln M + 5/2\, R \ln T - R \ln P + 4.967 - 16.024 + 8.757 \quad (4)$$

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(15) Cardoso and Giltay, *Arch. sci. phys. nat. Geneve*, **34**, 20 (1912)

TABLE VIII

CALCULATION OF THE ENTROPY OF AMMONIA

0–15°K., Debye function $h c \nu / k$ = 210	0.056
15–195.36°K., Graphical	10.16
Fusion 1351.6/195.36	6.919
195.36–239.68°K., Graphical	3.646
Vaporization 5581/239.68	23.29
Entropy of actual gas at boiling point	44.06 ± 0.10 cal./deg. per mole
Correction for gas imperfection	0.07
Entropy of ideal gas at boiling point	44.13

R = 1.9869 cal./deg. per mole. The values of all natural constants are those given in the "I. C. T."[6] The remaining entropy was evaluated by means of the equation

$$S = R \ln Q + RT \, \mathrm{d} \ln Q/\mathrm{d}T \qquad (5)$$

where $Q = pe^{-\epsilon/kT}$ summed over all states. p is the *a priori* probability and ϵ the energy of the state. For the rotational entropy the approximation

$$Q_R = \frac{1}{\sigma} \times \frac{8\pi^2}{h^3} \times (2\pi kT)^{3/2} \, (I_1 I_2 I_3)^{1/2} \qquad (6)$$

was used, where σ is the symmetry number and I_1, I_2 and I_3 are the principal moments of inertia. Therefore

$$S_R = R/2 \ln I_1 I_2 I_3 + 3/2 \, R \ln T + R \ln \frac{8\pi^2}{h^3} \cdot (2\pi k)^{3/2} + 3/2R - R \ln \sigma \qquad (7)$$

$$= R/2 \ln I_1 I_2 I_3 + 3/2 \, R \ln T - R \ln \sigma + 267.65 \qquad (8)$$

The moments of inertia have been taken from the observations of Wright and Randall[16] on the pure rotation spectrum of ammonia. Since the molecule is a symmetrical top

$$I_1 = I_2 = 2.782 \times 10^{-40} \text{ g. cm.}^2$$
$$I_3 = 4.33 \times 10^{-40} \text{ g. cm.}$$

The vibrational entropy was calculated by means of equation 5. Ammonia has four normal vibrational frequencies. ν_2 and ν_4 have double *a priori* weights. ν_1 and ν_3 are single. ν_1 = 3335 cm.$^{-1}$ [17] ν_3 = 948 cm.$^{-1}$ [18] ν_4 = 1631 cm.$^{-1}$ [17] ν_2 has never been observed spectroscopically. However, since it is known to be the largest frequency and does not contribute to the entropy below 298.1°K., an estimate of Howard[19] ν_2 = 3450 cm.$^{-1}$ was assumed.

From the above equations and data the entropy of the ideal gas at the boiling point was calculated to be 44.10 cal./deg. per mole. The contribution due to vibration was only 0.05 cal./deg. per mole. The value at 298.1°K. was found to be 45.91 cal./deg. per mole. These values are compared with the experimental results in Table IX.

In making the above calculations the nuclear spin entropy has been ignored. Since the hydrogen atom has a spin of $^1/_2$ and nitrogen a spin of 1 unit, the amount $R \ln 24$ = 6.31 cal./deg. per mole must be added to obtain the absolute entropy which has been included in Table IX for the sake of completeness. The values which do not include the nuclear spin contribution are the ones which should be used in ordinary thermodynamic calculations or compared with experimental values obtained from the ordinary application of the third law of thermodynamics.

TABLE IX

COMPARISON OF EXPERIMENTAL AND SPECTROSCOPIC ENTROPY VALUES OF AMMONIA

	Cal./mole/deg.			
	Spectroscopic		Experimental	
T, °K.	Absolute	Less nuclear spin entropy	Actual	Corrected to ideal state
239.68	50.41	44.10	44.06	44.13
298.1	52.22	45.91	...	45.94

As may be seen from Table IX the value obtained from the third law of thermodynamics is in excellent agreement with that obtained with the assistance of spectroscopic data.

Lewis and Randall[20] have given an equation for the free energy change in the reaction

$$1/2 \, N_2 + 3/2 \, H_2 = NH_3(g)$$

By means of this equation and the known entropies of nitrogen, N_2, $S_{298.1}$ = 45.79[21] and hydrogen, H_2, $S_{298.1}$ = 31.23[22] a value of 46.0 cal./deg. per mole is obtained for the entropy of ammonia at 298.1°K. This value is in excellent agreement with the experimental value 45.94 cal./deg. per mole.

We thank Dr. C. C. Stephenson for assisting with the measurements and many of the calculations.

Summary

The heat capacity of solid and liquid ammonia has been determined over their respective ranges from 15°K. to the boiling point. The melting and boiling points were found to be 195.36 and 239.68°K., respectively.

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(16) Wright and Randall, *Phys. Rev.*, **44**, 391 (1933).

(17) Shaefer and Matossi, "Das ultrarote Spektrum," Verlag von Julius Springer, Berlin, 1930, p. 250.

(18) Barker, personal communication to Wright and Randall.

(19) Howard, *J. Chem. Phys.*, **3**, 207 (1935).

(20) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., N. Y., 1923, p. 557.

(21) Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

(22) Giauque, *ibid.*, **52**, 4816 (1930).

The heat of fusion is 1351.6 cal./mole. The heat of vaporization at the boiling point is 5581 cal./mole.

The vapor pressure of solid and liquid ammonia has been measured and the data have been represented by the equations: solid ammonia 176.92 to 195.36°K. $\log_{10} P$ (int. cm. Hg) $= 1630.700/T + 9.00593$; liquid ammonia 199.26 to 241.59°K. $\log_{10} P$ (int. cm. Hg) $= -1612.500/T - 0.012311\, T + 0.000012521 T^2 + 10.83997$.

The molal entropy of the gas at the boiling point has been calculated by means of the third law of thermodynamics and the experimental data. The value found, 44.13 ± 10 e. u., is in excellent agreement with the value 44.10 e. u. calculated from spectroscopic data.

From band spectrum data the entropy of ammonia at 298.1°K. and 1 atmosphere was calculated to be 45.91 cal./deg. per mole.

The above entropy value, which should be used in ordinary thermodynamic calculations, does not include the nuclear spin entropy. The absolute entropy is 52.22 cal./deg. per mole.

BERKELEY, CALIF. RECEIVED NOVEMBER 16, 1936

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

The Relative Atomic Weight of Oxygen from Air and Water Determined by an Interchange Reaction

BY THOMAS O. JONES AND NORRIS F. HALL

An important difference in the composition of oxygen from the air and from water has been brought to light recently both in America and in Japan,[1] and this has been confirmed subsequently[2] by others. Various somewhat questionable assumptions and methods incident to the earlier papers have been discussed by Smith and Matheson,[2] but there seems little doubt of the reality of the difference, which readily accounts for certain otherwise unexplained results of workers other than the discoverers.[3] All of the results referred to above were obtained by burning elementary hydrogen with different sorts of oxygen, and electrolytic methods were generally employed to produce one or both of the gases.

We have now demonstrated this important effect by a method which involves neither electrolysis nor combustion, and which may prove practical for the preparation of large quantities of water abnormal as to its O^{18} content. The equilibrium between water and oxygen

$$2H_2O^{16} + O_2^{18} = 2H_2O^{18} + O_2^{16}$$

if established at low temperatures would, according to Dole,[1a] account for the observed difference. On the other hand, it is found, using the methods outlined by Urey and Greiff,[4] that at *high* temperatures the constant of this reaction closely approaches unity (at 1000°A., K is 1.0038, at 1500°A., K is 1.0002, at 2500°A., K is 1.0004), and that the departure of oxygen from a perfectly random atomic distribution in the three molecular forms is negligible in this temperature range.

Consequently, at 1500°A., for example, the O^{18}/O^{16} ratio of a sample of water in equilibrium with a large excess of air should be *the same* as in the air within 0.1 γ (water density at 25°) and within 0.09 γ at 2000°A. These differences are less than the probable error of the density determination. If then a sample of ordinary water were vaporized, heated with excess air and recondensed, its density should measurably increase, provided (a) air oxygen is really heavier and (b) there is an approach to equilibrium. The D/H ratio should remain unaffected.

Assuming that 7 γ is the correct value of the Dole effect for surface water, the equilibrium density increases to be expected are roughly

TABLE I

T, °A.	γ	Ref.
223	1.2	1a
273	4.8	1a
293	5.7	1a
373	6	2b
575	6.7	2b
1500	6.9	This paper
2000	6.91	

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(1) (a) Dole, THIS JOURNAL, **57**, 2731 (1935); *J. Chem. Phys.*, **4**, 268, 1936 (6 γ); (b) Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 36, 414 (1936) (7 γ).

(2) (a) Greene and Voskuyl, THIS JOURNAL, **58**, 693 (1936) (6 γ); (b) Hall and Johnston, *ibid.*, **58**, 1920 (1936) (6.6 γ); (c) Smith and Matheson, *Bur. Standards J. Research*, **17**, 625 (1936) (8.6 γ).

(3) (a) Hall and Jones, THIS JOURNAL, **58**, 1915 (1936) and the present paper; (b) Dole[1] and THIS JOURNAL, **58**, 580 (1936); (c) Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 419 (1936).

(4) Urey and Greiff, THIS JOURNAL, **57**, 321 (1935).

Experimental

In a first series of runs a large excess of cleaned air was passed through samples of ordinary water at room temperature with entirely negative results. (Average change of density in five runs lasting three to six days each $+0.3\ \gamma \pm 0.5\ \gamma$.)

In series 2 (4 runs at 100°) the results were also negative. Here air was bubbled through boiling water which was condensed and frozen out of the air stream and continuously returned to the flask. The average density change was $+0.15\ \gamma \pm 0.35\ \gamma$.

Since it seemed possible that the exchange might be promoted by catalysts of the type on which the reaction of oxygen and hydrogen is known to occur, steam and air were passed in series 3 over finely divided palladium, platinum, and platinum and silver oxide mixtures on asbestos. The results were again entirely negative. No significant changes in density were observed in nine days of treatment at temperatures up to 300°.

After this work was finished, we learned that W. Heinlen Hall and Johnston[2b] (p. 1922) had already reached the conclusion that "an exchange reaction between steam and molecular oxygen does not appear to be significantly catalyzed by platinum at 300°."

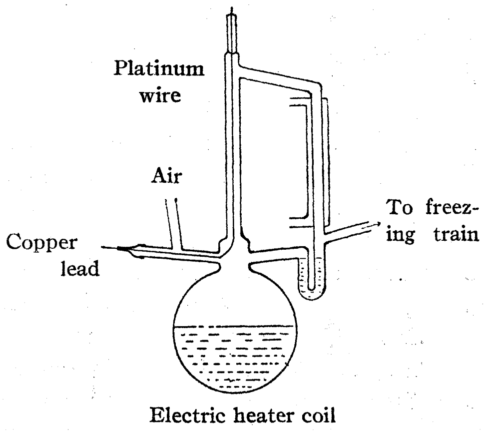

Fig. 1.—Equilibrator.

It now seemed quite likely that a much higher temperature would be required for activation. An apparatus was accordingly constructed which facilitated passing clean (dried) air together with steam over a platinum wire heated by an electric current to temperatures ranging from 1500°A. to 1800°A. (Fig. 1). A single strand of no. 30 wire about 25 cm. long was hung vertically under slight tension between bare copper leads in the center of an 8-mm. glass tube connected to a flask of water heated to 90–95°. The volume of the water samples was 100–110 cc. Air was admitted through a side-arm above the water surface. After passing the hot wire the bulk of the water vapor was condensed immediately from the air stream and returned to the original sample. That water which remained in the air stream was caught by means of a freezing train and also returned to the flask. The air flow was constant and limited to a rate such that nearly all the vapor could be removed in the freezing train. The loss of water in six days of treatment was less than 1%, a loss so small that it could not account for the changes in density observed. The quantity of air which passed over the wire with the water and the rate of reaction at 1800°A. were such that equilibrium was apparently established within three days. In each determination the time allotted was from two to three times this period. The rate of air flow was approximately 15 liters per hour. The temperature of the wire was determined by means of an optical pyrometer. In this series four samples of ordinary water were run under the regular conditions as described above with the wire heated to approximately 1800°A. Two other samples were run under exactly the same conditions as the first four except that the temperature of the wire was set at 1500 and 1600°A., respectively. Each sample was purified carefully and its density determined by means of a magnetic swimmer as described in a previous paper.[3a] The results are given in Table II.

TABLE II

Sample	T, °A.	Time, days	Density increase, $\Delta\gamma$
1a	1800	2.5	6.3
1b	1800	5	6.6
2	1800	4.5	6.9
3	1800	8	7.1
4a[a]	1800	7	7.1
4b	1800	3	7.3
Average of first four			7.0
5	1600	6	3.2
6	1500	6	3.3

[a] Sample 4a was replaced in the apparatus and equilibrated again for three days (becoming sample 4b). The slight increase in density was within the experimental error in the determination, indicating that equilibrium had been reached in the previous trial.

The results at lower temperatures (samples 5 and 6) were obtained with all other conditions unchanged and indicated that at 1600°A. about twenty-five days instead of three would be required for complete equilibrium and about sixty days at 1500°A. These data do not permit the calculation of the activation energy, because the limiting factor in attaining equilibrium at 1800°A. was that at any one instant the quantity of air in contact with the steam was limited. The great increase in the time required indicated, however, that the velocity of the reaction is greatly reduced by this reduction in temperature. From the fact that high temperature appears to be the necessary condition for the reaction, it may be presumed to depend on thermal dissociation rather than on activated adsorption.

This technique appears to make possible the easy preparation in a few days of considerable quantities of water whose slightly high density is due to oxygen alone. This aspect of the problem is now being studied further. An unknown sample of water may be normalized by this method (with respect to air oxygen rather than to a standard water) as an alternative to treatment with equilibrated carbon dioxide, sulfur dioxide, etc.[5]

We are indebted to the Research Committee of the University and to the Wisconsin Alumni Research Foundation for grants in aid of this work.

Summary

It has been found that the exchange equilibrium between water vapor and oxygen is rapidly established on a hot wire at 1800°A. and above, but much more slowly at lower temperatures. Water thus equilibrated with excess air increases in density by about 7 p. p. m., and the Dole effect is confirmed. Oxygen-abnormal water may be prepared conveniently by this method, and the oxygen isotope ratio of an unknown sample may be studied with its aid.

MADISON, WIS. RECEIVED DECEMBER 2, 1936

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[5] Dr. Charles H. Greene kindly writes as follows (December 22, 1936): "There is a small error in your result. The hot platinum in your apparatus brings the water vapor to the same isotopic composition as atmospheric oxygen. Water vapor, however, is slightly richer in O^{16} than the liquid water with which it is in equilibrium. Thus the liquid water in your apparatus, after equilibrium is attained, will be somewhat richer in O^{18} than atmospheric oxygen. From the results of Wahl and Urey, *J. Chem. Phys.* **3**, 411 (1935), I estimate the effect as 0.9 ± 0.3 p. p. m. This correction would bring your results into very good accord with our own."

If Dr. Greene's correction is accepted, our value of the Dole effect for liquid fresh water becomes 6.1 γ, assuming that complete equilibrium was reached.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 56]

The Oxybromides of Silicon

BY WALTER C. SCHUMB AND CAROLYN H. KLEIN

Although considerable information has been gathered concerning the oxychlorides of silicon,[1] little was known of the oxybromides of that element at the outset of this research. An investigation of the oxybromides of silicon was begun in 1934, with the object of isolating an homologous series of these compounds.

Of the various methods previously employed in the preparation of the oxychlorides, the ones which appeared most promising for adaptation to oxybromide preparation were the oxidation of the silicon tetrahalide, and the reaction of a mixture of oxygen and the halogen on silicon. In addition to these two successful methods, we have made studies of the oxidation of hexabromodisilane Si_2Br_6, silicobromoform $SiHBr_3$, and of Si_2OBr_6, as well as the effect of ozone and of silver oxide on silicon tetrabromide.

I. The Reaction of a Mixture of Oxygen and Bromine with Silicon and with Calcium Silicide.—The apparatus used in a study of the simultaneous effect of oxygen and bromine on silicon was similar to that used by Gattermann[2] for the preparation of silicon tetrabromide. A stream of oxygen, dried with calcium chloride, was bubbled through a trap of bromine (at 55°) at a rate of about 3 liters per hour (a velocity such that some oxygen bubbled through at the exit of the apparatus). The mixture of oxygen and bromine resulting was then passed over commercial silicon (averaging 97.5% Si) heated by a gas furnace to the desired temperature, about 700°. The product of the reaction was collected in a trap cooled in ice water.

The crude product was distilled fractionally, the excess bromine and silicon tetrabromide passing off first, followed by higher boiling material, which was collected up to 225° under a high vacuum. After repeated fractionation with an efficient column a separation of the compounds present in the mixture was effected. The combined results of two experiments, together with the formulas of the compounds isolated and identified by methods described below, are collected in Table I.

These substances all hydrolyze in the presence of moisture of the air, the speed being directly proportional to the volatility of the compound. They are miscible in all proportions with carbon tetrachloride, carbon disulfide, chloroform, and silicon tetrabromide. With the exception of the first and third, they have not been reported previously in the literature, and the two which were reported were prepared independently and by a different process.[3]

In order to determine the effect of a lower reaction temperature on the products formed, calcium silicide was used in another experiment in place of silicon, it being known that certain silicides react more readily with halogens at a lower temperature than does silicon itself. The reaction was carried out at a temperature of 180 to 200°, but in this case the product consisted almost wholly of hexabromodisilane, oxybromides being formed only in minute amounts. Evidently, in spite of an excess of oxygen, a Si–Si bond formed in preference to a Si–O–Si linkage.

Incidentally, the procedure just mentioned constitutes a far more satisfactory method of preparation of Si_2Br_6 than any hitherto described, as the yield is almost quantitative.

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[1] L. Troost and P. Hautefeuille, *Bull. soc. chim.*, [2] **16**, 243 (1891).

[2] L. Gattermann, *Ber.*, **22**, 186 (1889).

[3] H. Rheinboldt and W. Wisfeld, *Ann.*, **517**, 197 (1935).

TABLE I

Fraction	Appearance	Approx. no. g.	Approx. %	B. p., °C.	B. p., Mm.	F. p., °C.	Formula
I	Colorless liquid readily freezing to colorless tabular crystals	100	20.6	118	15	27.9 ± 0.1	Si_2OBr_6
II	Colorless liquid freezing in ice water to colorless solid	240	49.4	159	12	17.5 ± 0.2	$Si_3O_2Br_8$
III	Heavy white solid melting to colorless liquid	5	1.0	155	7	123–123.5	$Si_4O_4Br_8$
IV	Colorless liquid becoming very viscous on cooling and freezing to a glassy solid	60	12.4	122	<0.5	−91 ± 2°	$Si_4O_3Br_{10}$
V	Same	50	10.3	150	<0.5	−82 ± 2°	$Si_5O_4Br_{12}$
VI	Heavy colorless oil freezing in liquid air to glassy solid	30	6.2	160–180	<0.5	< −78°	Higher residue

II. The Reaction of Silicon Tetrabromide with Oxygen.—The silicon tetrabromide employed for the oxidation was prepared according to the method of Gattermann[2] by entraining bromine in a stream of carbon dioxide, and passing the resulting mixture over heated silicon. The oxidation of the tetrabromide was studied, early in the course of this research, between the temperatures 800 and 900°. It was found that, although the rate of oxidation was slow, the reaction proceeded all of the way to the formation of silica.

That further study of this reaction would be desirable was realized, but before this was accomplished a paper by Rheinboldt and Wisfeld[3] appeared, in which the results of their study of the same reaction are given. These workers found that the optimum temperature range for the formation of oxybromides is 670 to 695°; above this the reaction progresses to silica. Two oxybromides only were isolated by them, Si_2OBr_6 (m. p. began at 26.5°, but mostly at 28.5°, b. p. approx. 120° at 15 mm.) formed in small quantities, and $Si_4O_4Br_8$ (m. p. began at 121.5° but mostly at 123.5°, b. p. 170° at 15 mm.), formed in large quantities. The work of these authors was repeated and the results obtained are summarized in Table II.

TABLE II

Fraction	Product G.	Product %	Formula
I	18	14.4	Si_2OBr_6
II	37	29.6	$Si_3O_2Br_8$
III	38	30.4	$(SiOBr_2)_4$
IV	13	10.4	$Si_4O_3Br_{10}$
V	12	9.6	$Si_5O_4Br_{12}$
VI	7	5.6	Higher residue

From this table it can be seen that $(SiOBr_2)_4$, formed only as a trace by the simultaneous action of oxygen and bromine on silicon, is obtained in large amounts by the oxidation of silicon tetrabromide, a fact which is in agreement with the results reported by Rheinboldt and Wisfeld. It is apparent, however, that appreciable quantities of several other compounds, not reported by them, are also formed in the reaction. The purification and analysis of these compounds is described below.

III. Other Methods Studied

a. Oxidation of Hexabromodisilane, Si_2Br_6.—Since oxybromides may be prepared by the oxidation of silicon tetrabromide, it was thought that the oxidation of such substances as hexabromodisilane and silicobromoform might be of interest. The Si–Si bond present in Si_2Br_6 would be expected to break to admit oxygen more readily than the Si–Br linkage of the tetrabromide. When, however, oxygen was bubbled through the hexabromodisilane (prepared as described in Section I), which was heated to 230 to 250°, and the resulting mixture was passed back and forth through a tube heated electrically to the desired temperature, it was found that below 250° oxidation is negligible, and above this temperature silicon tetrabromide and silica are formed. In a typical experiment, with the Si_2Br_6 kept at 250°, the oxygen stream at a rate of 3 liters per hour, and the furnace temperature 300°, in the course of seven hours, 10 g. of Si_2Br_6 was decomposed to form silicon tetrabromide and silica. The reaction is evidently $2Si_2Br_6 + O_2 = 3SiBr_4 + SiO_2$.

b. Oxidation of Silicobromoform, $SiHBr_3$.—In 1868 A. J. Besson reported that in the preparation of silicobromoform from silicon and hydrogen bromide he noted the formation of a trace of material crystallizing in yellow platelets, and, since some air got into his apparatus during the reaction, he thought this substance probably was an oxybromide of silicon. Consequently it was decided to study the oxidation of silicobromoform in some detail in the hope of isolating this yellow material. The silicobromoform was prepared by passing a stream of hydrogen bromide over heated silicon.[4]

Dry air was bubbled at a rate of about two liters an hour through a solution containing 10 g. of silicobromoform, diluted with an equal volume of silicon tetrabromide to retard the reaction, and the exit tube for the gas was protected by a drying tube. The mixture in the trap was warmed gradually to 90°, at which temperature a deposit of the appearance of silica gradually precipitated, but no yellow color appeared. The reaction was accompanied by a slow evolution of hydrogen bromide, and distillation of the material in the trap showed the other products to be silicon tetrabromide, silicon dioxide, and a white solid (probably silicoformic anhydride), which exploded on impact. The formation of this could be explained as due to the hydrolysis of silicobromoform by the water formed as a product of the oxidation of silicobromoform.

c. The Reaction between Silver Oxide and Silicon Tetrabromide.—About 80 g. of silicon tetrabromide was refluxed slowly with 20 g. of silver oxide (dried for twenty-four hours at 75°, two hours at 120°, and one hour at 140°). The dark brown color of the silver oxide slowly disappeared, being replaced by the yellow color characteristic of silver bromide, and at the end of thirty hours the process was completed. Distillation of the product showed that the reaction had gone quantitatively according to the equation

$$2Ag_2O + SiBr_4 \longrightarrow 4AgBr + SiO_2$$

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[4] See W. C. Schumb and R. C. Young, THIS JOURNAL, **52**, 1464 (1930).

With the hope of stopping the action intermediately, the experiment was repeated with the tetrabromide diluted with an equal volume of carbon tetrachloride, and the temperature was kept at 80°. After forty hours of refluxing the reaction was completed, but in this case, too, the oxidation had progressed to silica.

d. The Ozonization of Silicon Tetrabromide.—The effect of ozone on silicon halides apparently has not been investigated previously. It was thought that such a reaction might prove interesting, since ozone forms an oxygen linkage between two carbons in certain organic compounds.

A stream of ozonized oxygen (8% ozone) was bubbled at a rate of about 3 liters an hour through a trap containing 30 g. of silicon tetrabromide. Since little or no effect was observed at room temperature, the trap was warmed gradually. After a period of two hours at 45°, the solution became pale orange in color, but, since the reaction was so slight, the temperature was gradually raised to 75°, whereupon the color deepened at a noticeable rate. Since this color is necessarily due to bromine set free, dilution with silicon tetrabromide must prevent the reaction of the bromine with the ozone from becoming violent at this temperature.

At the end of twenty hours a few cc. of bromine had collected, and a deposit of a gelatinous-looking solid appeared on the walls of the traps. Distillation showed the products of the reaction to be bromine, silica, and a trace of a high boiling oil. In the hope of increasing the amount of the latter, ozonization of silicon tetrabromide was repeated with the addition of a diluent. For this purpose carbon tetrachloride was chosen, since it is unreactive with ozone. After thirty hours, with a mixture of equal volumes of silicon tetrabromide and carbon tetrachloride kept at 40°, sufficient oxidation had occurred to warrant a distillation of the product. The results obtained, however, did not differ materially from those found in the first trial.

e. Thermal Decomposition of Si_2OBr_6.—Several articles relating to the formation of higher oxychlorides from Si_2OCl_6 appeared in 1876.[5] Since large quantities of Si_2OBr_6 were already available, the effect of oxygen on this compound was tried, the method employed being identical with that used for the oxidation of hexabromodisilane. It was found that there was no reaction below 200°, at which temperature an exceedingly slow action occurs, resulting in the formation of silicon tetrabromide and silica, together with a trace of a high boiling oil. The rate of decomposition gradually increases as the temperature is raised, but even at 260°, close to the boilingpoint of the oxybromide, the reaction is very slow.

Any reaction occurring obviously is not an oxidation process, since no bromine is set free; it evidently proceeds for the most part according to the equation $2Si_2OBr_6 = 3SiBr_4 + SiO_2$, and to a very small extent in this manner: $4Si_2OBr_6 = 3SiBr_4 + Si_5O_4Br_{12}$. In either case the oxygen used plays no part in the process and any inert gas should serve as well; as was shown experimentally to be the case.

Purification of Products and Freezing Point Determinations.—The purification of fractions II, IV and V (Table I) was effected entirely by repeated fractional distillations. The type of column which proved most satisfactory was a two-foot (60 cm.) vapor-jacketed column of the Podbielniak type, with a solid glass spiral fitted into a Pyrex tube (outside diameter 8 mm.). For the purification of fraction I partial crystallization from its own liquor was used, as well as distillation. In the case of number III, fractional distillation was followed by two crystallizations from carbon disulfide, the crystals being separated from the solution in the absence of moisture by means of a sintered glass plate, and washed with fresh solvent.

Of the physical constants of the compounds obtained tabulated in Table I, the freezing points were quite sharp with the first three compounds, but some difficulty was experienced in obtaining accurate values in the case of the last two compounds. These liquids became increasingly viscous on cooling to the temperature of solid carbon dioxide, and upon immersion in liquid air froze to a colorless solid with a glassy appearance. Whether this was due to polymerization of the molecules on cooling is not known, but seems probable. Approximate freezing point determinations of these two compounds were made by immersion in alcohol cooled with liquid air.

Methods of Analysis and Molecular Weight Determinations.—In the analytical work required to establish the composition of the oxybromides prepared in this work, both the bromine and the silicon content were determined, gravimetrically, the former as silver bromide and the latter as silica. The percentage of oxygen was calculated by difference.

Molecular weight values were determined by the Beck-

TABLE III

ANALYTICAL DATA AND MOLECULAR WEIGHTS

Fraction	Si, %	Br, %	Mean ratio Si:O:Br	Mol. wt. (by f. p. method)
I		87.21		
	10.20	86.85	2:0.99:5.98	597
	10.17	86.77		573
Si_2OBr_6	10.14	86.96	2:1:6	552
II	11.23	84.50		838
	11.06	84.62	3:2.03:7.90	836
	11.11	84.45		795
$Si_3O_2Br_8$	11.11	84.65	3:2:8	756
III	13.46			895
	13.53	79.50		790
	13.66	79.15	1:0.92:2.05	856
$Si_4O_4Br_8$	13.72	78.43	1:1:2	816
IV	11.91	83.43		
	11.64	81.43	4:2.95:9.97	989
	11.70	83.39		930
	11.54	83.31		
$Si_4O_3Br_{10}$	11.67	83.33	4:3:10	959
V	12.03	82.33	5:4.05:12.00	1299
	12.02	82.46		1232
				1223
$Si_5O_4Br_{12}$	12.03	82.47	5:4:12	1163
VI	12.14	82.15		
	12.18	82.10	6:5.0:14.4	[a]
$Si_6O_5Br_{14}$	12.28	81.85	6:5:14	1367

[a] The results on this fraction, while less complete and less accurate than the preceding five, strongly indicate the presence of the oxybromide $Si_6O_5Br_{14}$.

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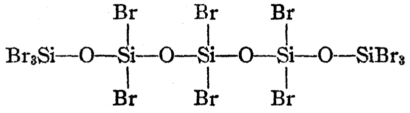
[5] L. Troost and P. Hautefeuille, *Ann. chim. phys.*, [5] **7**, 453 1876).

mann freezing point lowering method. Ethylene bromide (Eastman Reagent) which was used as the solvent in the molecular weight work, was dried by allowing it to stand over phosphorus pentoxide for twenty-four hours, after which it was fractionally distilled from fresh drying agent, giving a sample with a boiling point of 129.5 to 130°. The cryoscopic constant of ethylene bromide was taken as 12.50° per mole per 1000 g. of solvent.[6]

The fractions given in the following tabulation refer to those of Table I. The same weight of solvent, 54.73 g. (the contents delivered by a calibrated pipet), was used in each molecular weight determination.

The simplest conceivable oxybromide, $SiOBr_2$, like the corresponding chloride, is probably incapable of existence outside the vapor state, and in the liquid state polymerizes to $(SiOBr_2)_4$, or $Si_4O_4Br_8$. With the exception of $(SiOBr_2)_4$, the compounds are all members of the series of general formula $Si_nO_{n-1}Br_{2n+2}$, of which series $SiBr_4$ itself might be considered as the first member. Although there is evidence of a ring structure for $(SiOBr_2)_4$, the other substances are most probably straight-chain compounds, with an oxygen atom linked between each Si atom, such as



$$Br_3Si{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}SiBr_3$$

Compounds containing the terminal linkage $-\underset{\displaystyle Br}{\underset{|}{Si}}{=}O$, although logically to be expected, apparently are not realized.

Summary

1. The following series of silicon oxybromides was prepared: $(SiOBr_2)_4$, Si_2OBr_6, $Si_3O_2Br_8$, $Si_4O_3Br_{10}$ and $Si_5O_4Br_{12}$, definite indication of the existence of $Si_6O_5Br_{14}$ (and perhaps of higher oxybromides) also being shown. All but the first compound belong to the homologous series $Si_nO_{n-1}Br_{2n+2}$. The compounds all hydrolyze readily in the presence of moisture, the rate of hydrolysis decreasing with a decrease in volatility. They are miscible in all proportions with CS_2, CCl_4, $CHCl_3$ and $SiBr_4$.

With the exception of the first two compounds (which were prepared independently in the present work, and by independent methods) these substances have not been reported previously, nor has as complete a series of any other silicon oxyhalides been prepared.

2. With the hope of obtaining oxybromides of silicon, the following reactions were studied: A, the simultaneous reaction of oxygen and bromine, both with silicon and with calcium silicide; B, the reaction of silicon tetrabromide with oxygen; C, the oxidation of hexabromodisilane; D, the oxidation and the thermal decomposition of Si_2OBr_6; E, the reaction of silicobromoform with oxygen; F, the effect of silver oxide on silicon tetrabromide; G, the ozonization of silicon tetrabromide. The first two methods resulted in the formation of large quantities of oxybromides. In no other case were appreciable quantities of oxybromides formed, the reaction progressing all of the way to silicon dioxide.

CAMBRIDGE, MASS.

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[6] "International Critical Tables," Vol. IV, p. 183.

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

The Electrode Potential of the Iodine–Iodate Electrode at 25°[1]

BY WALTER O. LUNDBERG,[2] CARL S. VESTLING[3] AND J. ELSTON AHLBERG

The purpose of the present investigation has been to gather additional data necessary to determine more closely the standard potential at 25° for the electrode reaction

$$^1/_2I_2(s) + 3H_2O(l) = IO_3^- + 6H^+ + 5E^-$$

The value of the standard potential available until now is based upon the work of Sammet,[4] but several experimental factors contribute to considerable uncertainty in his results. The most important of these is that he measured the potential of the iodine–iodate electrode at 25° against a normal calomel potassium chloride electrode maintained at 18°. Furthermore, the liquid potentials with which he had to deal were relatively high, ranging up to 0.034 volt. The results of Sammet have been recalculated employing the activity coefficients of hydrogen ion as given by Lewis and Randall[5] and those of iodic

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(1) In part from a dissertation submitted by Walter O. Lundberg to The Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

(2) Hormel Foundation Fellow in Chemistry, 1930–1934.

(3) Patrick Garvan Fellow in Chemistry, 1934–.

(4) Sammet, *Z. physik. Chem.*, **53**, 665 (1905).

(5) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

acid as measured by Abel, Redlich and Hersch.[6] The thermocouple effect existent in the cell (+0.005 volt) was calculated from the data of Coggeshall[7] and the proper correction applied. The liquid potentials as calculated by Sammet were employed. The voltage of the normal calomel electrode at 25° was taken to be −0.2822 volt as given by Lewis and Randall.[5] The recalculated results of Sammet are summarized in Table I. Other reviewers[5,8] of the work of Sammet have neglected to take into account the thermocouple effect.

TABLE I

EXPERIMENTAL RESULTS OF RESEARCH BY V. SAMMET[4]: ELECTRODE POTENTIAL OF THE IODINE–IODATE ELECTRODE AT 25°

Reaction: $^1/_2I_2(s) + 3H_2O(l) = IO_3^- + 6H^+ + 5E^-$
Cell employed: Pt, $I_2(s)$, HIO_3 (*xm*), KCl(*xm*), KCl(*N*), HgCl, Hg. Pt, $I_2(s)$, HIO_3(*xm*) at 25°. KCl(*N*), HgCl, Hg at 18°

Concn., mole per liter	0.1	0.01	0.001	0.001[a]
Voltage **E**, observed	−0.784	−0.710	−0.630	−0.666
Mean deviation of **E**	0.001	0.001	0.001	0.001
Liquid junction potential	−0.034	−0.034	−0.034	0.000
Standard potential **E**°	−1.187	−1.190	−1.191	−1.193

[a] For this single measurement the liquid junction was between 0.001 *m* iodic acid and 1 *N* potassium chloride.

In the present investigation the standard potential was determined using inert electrodes of platinized platinum in contact with saturated solutions of iodine in iodic acid at 0.1 and 0.01 *M* concentrations. The potential of this electrode was measured against a hydrogen electrode (both at 25°) in which the concentration of the hydrochloric acid was the same as that of the iodic acid at the other electrode. The liquid junction is of the most simple type and its potentials should be only a few millivolts.

The data presented here when combined with those available in the literature do not at present allow an ultimate evaluation of the standard electrode potential. The principal reason for being unable to do this lies in the fact that the simple expression of Lewis and Sargent[9] (later derived by MacInnes and Yeh[10]) for the potential of the liquid junction existent in the cell employed for these measurements is apparently not strictly applicable. When this expression is employed a discrepany of 0.004 volt exists between the standard potentials calculated from the measurements at 0.1 and 0.01 *M*. The activity coefficients available[6] are strictly only applicable at the freezing points of the corresponding solutions. It is of course possible that the activity coefficients are sufficiently different at 25° to account for the discrepancy. The employment of Planck's equation[11] for the liquid junction potential gives standard potentials which agree very well. However, it is not safe to assume that the expression of Planck is applicable since its derivation restricts its use to extremely dilute solutions. It is also important to note that in the calculation of the standard potential (exclusive of the liquid potentials) it is necessary to assume that the activity of the hydrogen ions at the hydrogen electrode and at the iodine–iodate electrode are the same. Fuoss and Kraus[12] have shown that the electrical conductivities of dilute solutions of iodic acid can be explained upon the basis of the interionic attraction theory (Debye–Hückel) provided one assumes that iodic acid is not completely ionized. They find that its dissociation constant (expressed in terms of activity) must be chosen to be 0.17 to give agreement with experiment. MacInnes and Yeh[10] show that the formula of Lewis and Sargent requires that the electrolytes be ionized completely and that the activities of hydrogen ion be the same in the solutions of iodic and hydrochloric acids. Calculations based upon the above equilibrium constant indicate that at 0.1 *M* the hydrogen ion activities differ to such an extent that the liquid potential cannot be calculated with exactness. However, at 0.01 *M* the equilibrium constant indicates that iodic acid may be considered almost completely ionized (hence the hydrogen ion activities almost equal) and to such an extent that the liquid potential is probably given by the equation of Lewis and Sargent with an accuracy of 0.001 volt.

On several occasions the question has been raised whether the several possible reactions of iodine and its derivatives with water might make for a number of electrode reactions which would interfere with the measurement of the potential of the main reaction in which one is interested. For that reason it is well to emphasize that as long

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(6) Abel, Redlich and Hersch, *Z. physik. Chem.*, **170A**, 112 (1934).
(7) Coggeshall, *ibid.*, **17**, 62 (1895).
(8) Gerke, *Chem. Rev.*, **1**, 377 (1925).
(9) Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).
(10) MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).
(11) Planck, *Ann. Physik*, **40**, 561 (1890).
(12) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

as all of the substances reacting at *any* electrode are in chemical equilibrium, the measured potentials for the main reaction and all other secondary reactions are the same. Furthermore, if the concentrations of the reactants and products of the secondary reactions are known, their respective standard potentials may be calculated. The above statement may be proved readily from a thermodynamic standpoint by employment of the free energy function or by the use of activities. It is important to note that the free energy changes involved when iodine is added to the iodic acid solutions used in the present measurements are such that the iodic acid concentrations are not appreciably changed. From a practical standpoint they are unchanged.

Experimental

The measurements were carried out in an air thermostat. The temperature within the thermostat, as read from an accurately calibrated mercury thermometer, could be maintained constant at 25° to within 0.02° over periods of several hours. When the thermostat was unattended in the intervals between the periods of observation, temperature deviations of 0.1° were noted. All potential measurements were made with a Leeds and Northrup type K potentiometer. The sensitivity of the galvanometer was such that with the solutions at concentrations of 0.01 *M* or greater, the potential could be easily read with an accuracy of 0.0001 volt.

The hydrogen electrode vessel was essentially the same as that described by Lewis, Brighton and Sebastian.[13] It was constructed of Pyrex glass and contained two electrodes of platinized platinum. In preparing the electrodes the platinum was thoroughly cleaned with strong chromic acid solution and hot concentrated nitric acid, and then was heated almost to white heat in the flame of a blast lamp. A thin coating of platinum black was then applied according to the procedure recommended by Clark.[14] The platinum leads were sealed into the glass, and at no time was mercury used as a seal for either the hydrogen or the iodine–iodate electrodes.

The iodine–iodate electrode vessel was so constructed that it could be filled completely with solution thus completely excluding air. It contained two electrodes of platinized platinum; the platinum coating was of such thickness that the glint of the underlying metal could be seen. In setting up the cell for a set of measurements, a saturated solution of iodine in iodic acid solution was introduced into the cell. None of the stopcocks in the iodine–iodate electrode vessel was greased.

The two electrode vessels were connected by means of an all-glass bridge containing a three-way stopcock. The third arm of the stopcock was used as a drain and also as a point of connection for the calomel cell which was used to check the hydrogen electrode.

Electrolytic tank hydrogen was used for all measurements. The hydrogen was purified by bubbling through a concentrated solution of potassium hydroxide, passed over a copper gauze heated to 450° by an electric furnace, and then through a soda lime tower.

Conductivity water was used in the preparation of all solutions. C. P. iodine was purified by treatment with potassium iodide to remove other halogens, and subsequently by several sublimations.

The iodic acid solutions used for the first set of measurements (series A-1, and A-2) were prepared from Kahlbaum best grade of iodic acid. The most concentrated (0.0950 *M*) solution (used in series A-1) was standardized with standard sodium hydroxide for its hydrogen ion concentration and with standard sodium thiosulfate for its iodate ion concentration. The values for duplicate determinations of the concentration of each ion did not differ by more than 0.1%. The average value of the concentration of each of the ions agreed exactly to the fourth decimal. The solution used for series A-2 (0.01 *M*) was made up by accurate dilution of the 0.0950 *M* solution.

The iodic acid used for the second set of measurements (series B-2) was prepared by oxidation of highly purified iodine with fuming nitric acid and hydrogen peroxide. The iodic acid was purified by several crystallizations from aqueous solutions by the addition of concentrated nitric acid. The crystals obtained were dried (for twelve hours) by vacuum desiccation at room temperature. From this white crystalline material a 0.1060 *M* solution was prepared. Triplicate analyses for hydrogen ion had a mean deviation of 0.2%. Duplicate analyses for iodate ion differed by 1.0%. The discrepancies are largely due to the fact that inadequate volumes were available for the titrations. The average value of the hydrogen ion concentration was 0.1063 *M* and that of iodate ion 0.1057 *M*. The solution used for series B-2 (0.01000 *M*) was made up by accurate dilution of the 0.1060 *M* solution.

The solid iodic acid prepared for series B-2 was further purified by recrystallization from aqueous solution by concentrated nitric acid. The crystals were dried for forty-eight hours by vacuum desiccation at room temperature. This solid (perfectly white) iodic acid was used for the third set of measurements series C-1, and C-2. A 0.0954 *M* solution was prepared. Triplicate analyses for hydrogen ion had a mean deviation of less than 0.07%. Triplicate analyses for iodate ion had a mean deviation of less than 0.02%. The average value of the hydrogen ion concentration was 0.0956 *M* and that of the iodate ion 0.0953 *M*. While this discrepancy may be due to the presence of a trace of nitric acid it has been attributed to differences in the standard reagents. The value 0.0954 *M* is a weighted average of the last two figures.

The solutions of hydrochloric acid were made up from Baker's Analyzed C. P. concentrated hydrochloric acid. These stock solutions were standardized against pure sodium carbonate and against silver chloride (gravimetrically). The concentrations given by the two methods agreed to within 0.1%.

All other chemicals used either directly or indirectly were of the highest quality.

Comparison of the hydrogen electrodes with freshly prepared calomel electrodes indicated that the hydro-

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[13] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

[14] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 1928.

TABLE II

EXPERIMENTAL RESULTS OF THIS RESEARCH (L., V. AND A.)

Electrode Potential of the Iodine–Iodate Electrode at 25°

Unit of potential, international volt

Reaction: $^1/_2I_2(s) + 3H_2O(l) = 5/2H_2(g) + H^+ + IO_3^-$

Cell employed: Pt, $I_2(s)$, $HIO_3(xM)$, $HCl(xM)$, $H_2(g)$, Pt

Series	A-1	C-1	A-2	B-2	C-2
Concn., mole per 1000 g. water	0.0950	0.0954	0.01000	0.01000	0.01000
Voltage **E** p. p. H_2 76.0 cm. Hg	−1.1621	−1.1618	−1.1425	−1.1432	−1.1429
Mean dev. of **E**	0.0001	0.0001	0.0002	0.0001	0.0003
Number of sets of voltage observations	10	11	14	4	14
Number of times solutions replaced	3	1	4	3	4
Hours allowed for equilibrium	2	6	10	10	10
Maximum hours observed	16	96	20	18	72
Standard potential $\mathbf{E}^0$ from Lewis and Sargent equation	−1.1997	−1.1994	−1.1947	−1.1954	−1.1951
Standard potential $\mathbf{E}^0$ from Planck equation	−1.1937	−1.1934	−1.1936	−1.1943	−1.1940

gen electrodes functioned properly during the measurements.

It was necessary to allow the iodine–iodate cells to stand for some time before equilibrium was established. For the 0.1 *M* solutions equilibrium was established fairly rapidly (less than two hours). For the 0.01 *M* solutions the rate of attainment of equilibrium was less rapid (less than ten hours). The periods of time that the potentials of the cells were observed and their fluctuations are given in Table I. At 0.001 *M* the cells would not give reproducible results and are consequently not reported. An attempt was made to make similar measurements on the bromine–bromate electrode but due to lack of reproducibility of potentials the investigation was discontinued.

The conditions under which the liquid junction was established were varied considerably in order to study its reproducibility. In most of the measurements the liquid junction was formed at the ungreased three-way stopcock which connected the electrode vessels. Readings were taken with the stopcock open and closed. When this stopcock was left open another stopcock in the bridge to the hydrogen electrode vessel was kept closed to prevent motion of the liquid in the bridge and to preclude the possibility of diffusion of iodine into the hydrogen electrode vessel. Readings taken with the three-way stopcock open remained constant for relatively long periods of time and were readily reproduced when the bridge was flushed and refilled with fresh solutions. Readings taken with the three-way stopcock closed changed after a few minutes, probably because of composition changes of the solutions forming a thin film in the closed stopcock. When the stopcock was again flushed the original readings were obtained.

The cell employed to measure the electromotive force of the iodine–iodate couple may be represented as

$$\text{Pt}, I_2(s), HIO_3(xm), HCl(xm), H_2(g), \text{Pt}$$

The total cell reaction is

$$\text{(A)} \quad ^1/_2I_2(s) + 3H_2O = 5/2H_2(g) + H^+ + IO_3^-$$

The measured potential[15] at 25° is given by

$$\mathbf{E} = \mathbf{E}^\circ + \mathbf{E}_L - (0.05913/5) \log (H_2)^{5/2} (H^+)(IO_3^-)$$

As discussed before it is difficult to evaluate the liquid potential term. The liquid potential for such a junction is usually given by

$$\mathbf{E}_L = +0.05913 \log \frac{\Lambda_{H^+} + \Lambda_{Cl^-}}{\Lambda_{H^+} + \Lambda_{IO_3^-}}$$

Planck[11] was the first to give the theory of such a liquid junction, but his equation must be regarded as only strictly applicable at infinite dilution. Planck's expression is the same as that above, with the conductivity terms being those at infinite dilution. The liquid potential given by Planck's expression is the same (+0.0025 volt) for the 0.1 and 0.01 *M* solutions. Consequently the standard potentials calculated by Planck's equation are in excellent agreement. The Lewis and Sargent[9] equation derived by MacInnes and Yeh[10] is applicable at all concentrations provided both electrolytes are completely ionized and the activities of the common ion are the same in both solutions. The Lewis and Sargent equation is that given above with the conductivity terms being those at the concentrations employed. The equivalent conductivities employed are those given in the "International Critical Tables," 1929. When employed in the Lewis and Sargent equation these values give +0.0034 and +0.0083 volt at 0.01 and 0.1 *M* concentrations, respectively.

The products of the activities of the hydrogen ions and iodate ions were calculated from the activity coefficients of iodic acid.[6]

The experimental results are tabulated in Table II.

It is estimated that the averages of the directly measured potentials at each concentration are accurate to about 0.0005 volt. The incomplete dissociation of iodic acid at 0.1 *M* is consistent with the discrepancies noted in the standard potentials calculated from the measurements at

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[15] The conventions employed are those given by Lewis and Randall, ref. 5.

0.01 and 0.1 *M* concentrations. Since iodic acid may be considered almost completely dissociated at 0.01 *M*, it is believed that −1.195 volts should be accepted for the present as the standard potential for the iodine–iodate reaction (A). It is estimated that the probable error of this last value is about 0.002 volt.

Free Energy and Heat of Formation of Iodate Ion.—From the standard electrode potential given by this research one may calculate the standard free energy change at 298.1°K. for the reaction

$$^1/_2I_2(s) + 3H_2O(l) = 5/2H_2(g) + H^+ + IO_3^-$$
$$\Delta F^\circ_{298\cdot1} = -5 \times 23066 \times (-1.195) = 137{,}819 \text{ calories}$$

Gordon[16] has computed the entropy of water from spectroscopic data and with the heat of formation of water[17] and the entropies of hydrogen[18] and oxygen,[19] he calculates the free energy of formation of water

$$3H_2 + 3/2\,O_2 = 3H_2O(l) \quad \Delta F^\circ_{298\cdot1} = -170.070 \text{ calories}$$

By subtraction of the last reaction from the preceding reaction one may calculate the free energy of formation of iodate ion.

$$^1/_2I_2(s) + 3/2\,O_2 + {}^1/_2H_2 = H^+ + IO_3^- \quad \Delta F^\circ_{298\cdot1} = -32{,}251$$

The entropies of iodine[20] and of iodate ion[21] are known in addition to those of hydrogen and oxygen. The entropy change in this reaction is 76.20 cal./deg. and combination with the value for the free energy change gives for the heat of formation of iodate ion $\Delta H^\circ_{298\cdot1} = -54{,}966$ calories. It is well to note that this value at 298.1°K. is in good accord with the value at 291°K. given in the summary by Bichowsky and Rossini.[22]

The authors wish to thank Professor W. M. Clark and Dr. E. G. Ball of the Physiological Chemistry Department of The Johns Hopkins University for helpful advice.

Summary

The electrode potentials of the iodine–iodate electrode reaction have been measured at several concentrations and its standard electrode potential evaluated

$$^1/_2I_2 + 3H_2O = IO_3^- + 6H^+ + 5E^- \quad E^\circ_{298\cdot1} = -1.195 \text{ volts}$$

The free energy, entropy and heat of formation of iodate ion have been evaluated.

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(16) Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(17) Rossini, *Bur. Standards J. Research*, **6**, 1 (1933).

(18) Giauque, THIS JOURNAL, **52**, 4831 (1930).

(19) Johnston and Walker, *ibid.*, **55**, 172 (1933).

(20) Giauque, *ibid.*, **53**, 513 (1931).

(21) Ahlberg and Latimer, *ibid.*, **56**, 858 (1934).

(22) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, 1936.

BALTIMORE, MD. RECEIVED NOVEMBER 5, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Catalytic Decomposition of Hydrogen Peroxide by Aluminum Oxyiodide Hydrosols

BY ARTHUR W. THOMAS AND BENJAMIN COHEN

The catalytic decomposition of hydrogen peroxide by aluminum oxyiodide hydrosols[1] has been investigated for the first time for the purpose of studying the changes of the iodide ion concentration in these colloidal systems under various conditions.

This particular reaction was chosen for the following reasons: (1) It has been shown by several investigators that over a large range of iodide concentration, the decomposition of hydrogen peroxide in neutral solution is strictly proportional to the iodide ion concentration. (2) Hydrous aluminum oxide itself, and also in the presence of several potassium salts used in this study, had no appreciable catalytic effect upon hydrogen peroxide. (3) The decomposition of hydrogen peroxide by the sols was homogeneous and first order.

The *p*H values of the hydrosols were about 5.6 and increased to a maximum of *p*H = 8 upon the addition of certain potassium salts. In this range of *p*H, the steady state function for the iodide–iodine couple as investigated by Abel[2] and Liebhafsky[3] indicates that less than 1% of the total iodide present in our hydrosol systems will be removed to form iodine or tri-iodide ion. In

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(1) Perhaps a better name is "basic aluminum iodide" hydrosols. They are known also as "aluminum oxide" hydrosols with sorbed and contra iodide ions.

(2) Abel, *Z. physik. Chem.*, **136**, 161 (1928).

(3) Liebhafsky, THIS JOURNAL, **54**, 1792 (1932).

TABLE I

PREPARATION AND PROPERTIES OF THE SOLS

Sols	Temp. and time of preparation		Time of dialysis, days	I content[a]	Al content[a]	Ratio $\frac{Al}{I}$	pH	P. F.[b]
1	Boiling	12 hrs.	10	0.290	39.1	135	5.61	1.8
2	Boiling	7 hrs.	12	.137	15.3	112	5.63	2.2
3	Boiling	7 hrs.	18	.244	40.4	166	5.68	2.7
4	90°	7 hrs.	10	1.570	134.5	87	5.65	4.0
5[c]	25°	7 days	14	0.040	30.7	768	5.66	1.15
6	Boiling	7 hrs.	11	2.234	277.7	124	5.78	3.5
7[d]	Boiling	7 hrs.	0	13.22	321.2	24	4.86	..
8	Boiling	7 hrs.	10	1.025	136.1	132	5.75	3.0

[a] In milliequivalents per liter. [b] P. F. = "Promotion Factor," defined as the ratio of the observed velocity constant to the velocity constant calculated for a system where all the iodide is free or unbound. [c] Sol 5 was rather unstable and began to precipitate after standing three weeks. [d] Sol 7 was used for e. m. f. measurements only. Iodide ion activities of sols 6, 7 and 8 were 7.9, 54 and 3.6 × 10^{-4}, respectively.

this sense, the reaction was independent of the pH changes encountered in the present investigation.

Preparation of Hydrosols.—The hydrosols used in this investigation were prepared by the action of dilute hydriodic acid solutions upon aluminum amalgam in all details as previously described.[4] The description of these sols is given in Table I.

Other Materials Used.—Merck "Superoxol" was distilled under reduced pressure in a previously steamed "Pyrex" glass apparatus and stored in paraffined containers. The 0.1 *N* potassium salt solutions were prepared from suitable purified materials and they had the following pH values: iodide 7.01, nitrate 6.48, acetate 6.42, sulfate 6.12 and tartrate 6.66; the pH values of the acetate and tartrate are lower than those found in solutions of these "neutral" salts owing to deliberate addition of some acetic and tartaric acids, respectively.

Measurement of H^+ and I^- Activities.—Electrode measurements were made at 25 ± 0.05°. The hydrogen ion activity of the sols was measured by means of the quinhydrone electrode using a saturated potassium chloride calomel half cell as the additional element. The platinized platinum hydrogen gas electrode was used when the pH value was near 8.

Iodide ion activity measurements were made with silver–silver iodide electrodes made up according to Owen.[5] Electrodes made in this way are reported to be reproducible to ±0.05 mv.[5,6] and have been found reliable in very dilute solutions.[6] In this work, silver–silver iodide electrodes were indistinguishable in 0.1 *N* potassium iodide, the precision of the potentiometer system being ±0.1 mv. In undialyzed sols, duplicate electrodes agreed within ±0.2 mv., whereas in dialyzed sols they performed less satisfactorily with variations frequently as large as one millivolt. The technique of measurement was as follows: a constant volume of salt solution (2 cc.) was added to 20 cc. of sol, the mixture shaken and two silver–silver iodide electrodes, fitted in a rubber stopper, were immersed in the solution. The cell was allowed to equilibrate overnight at 25°; using a saturated potassium chloride calomel cell as the additional element, the e. m. f. of the cells was then measured at three-hour intervals until constant readings were obtained.

The normal electrode potential of the silver–silver iodide electrode was taken as $E^0 = 0.151$ volt, the average of three values reported in the literature.[5,7,8]

Method of Measurement of the Velocity of Decomposition of Hydrogen Peroxide.—Since in the present work, the greatest iodide content of the reaction system was two milliequivalents per liter, it was found possible to employ the titration method, determining the concentration of hydrogen peroxide during the course of the reaction by titration with potassium permanganate solution.

The procedure was usually as follows: a 100-cc. portion of hydrosol was pipetted into a previously steamed 200-cc. "Non-Sol" glass bottle. A measured volume of salt solution (usually 10 cc.) was added. The mixture was shaken and then kept overnight in a water thermostat at 25 ± 0.005° to ensure equilibrium. To start the reaction a measured volume of hydrogen peroxide solution was added to the mixture. At various time intervals, a 25-cc. portion of the reaction mixture was withdrawn and permitted to flow into a 250-cc. Erlenmeyer flask containing 125 cc. of an ice and sulfuric acid mixture.[9] The oxygen was expelled from the reaction system before withdrawing aliquots by gently shaking the bottle in the thermostat, then removing the bottle from the thermostat and shaking the mixture violently for about ten seconds. Except when the reaction was relatively slow, the time of sampling was recorded as the time when the pipet was half emptied. Titration with potassium permanganate followed immediately.[10]

In some of the measurements (sols 1, 2, 3 and 6) the procedure was slightly changed. After the reaction had been started, 25-cc. portions of the reaction mixture were transferred into separate 250-cc. wide-mouthed glass-stoppered "Pyrex" flasks which had been well steamed previously.

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(4) Thomas and Tai, THIS JOURNAL, **54**, 841 (1932).

(5) Owen, *ibid.*, **57**, 1526 (1935).

(6) Keston, *ibid.*, **57**, 1671 (1935).

(7) Pearce and Fortsch, *ibid.*, **45**, 2852 (1923).

(8) Gerke, *ibid.*, **44**, 1684 (1922).

(9) "Stopping" the reaction by the ice–sulfuric acid mixture was effective due to dilution and cooling. Considering the fact that in acid solution, hydrogen peroxide will oxidize I^- to I_2, the titer of hydrogen peroxide would decrease 1% in the most unfavorable cases were this reaction to go to completion.

(10) No correction was made for the iodine formed during the titration of hydrogen peroxide by potassium permanganate since the error involved was within the precision of the experiment.

At various time intervals an ice and sulfuric acid mixture was poured into the vessels and titrated immediately with permanganate.[10] Although the second method obviated the necessity of withdrawing the entire reaction mixture from the thermostat to expel the oxygen, the precision was practically unaltered.

The concentration of hydrogen peroxide at the beginning of the reaction was adjusted to 0.5 N in the case of systems having 1.5 or more milliequivalents per liter of iodide. In other cases an initial concentration of 0.3 N hydrogen peroxide was used.

Measurements upon a given hydrosol were completed as soon as possible in order to avoid errors arising from the changes which these hydrosols undergo upon aging even at room temperature. During a series of measurements the reaction mixture was kept in the dark.

The reaction followed the first order equation

$$K = \frac{2.303}{t} \log \frac{a}{(a - x)}$$

where a was taken as the number of cc. of potassium permanganate solution used in the first titration and $(a-x)$ the number of cc. of potassium permanganate used after the reaction had progressed t minutes.

The precision of this method may be seen from some representative experiments which follow:

Sol (8) In absence of salts

t, min.	Cc. $KMnO_4$	$K \times 10^3$
0	40.07	..
59.26	32.50	3.55
128.8	25.20	3.60
214.9	18.35	3.64
	Av.	3.59[a]

[a] A duplicate series of measurements yielded the average value of $K = 3.61 \times 10^{-3}$.

Sol (8) In presence of 0.0087 N potassium tartrate

t, min.	Cc. $KMnO_4$	$K \times 10^3$
0	38.81	..
188.0	30.64	1.26
352.6	24.95	1.25
578.2	18.99	1.24
	Av.	1.25

1.544×10^{-3} N KI in presence of 0.06 N K_2SO_4

t, min.	Cc. $KMnO_4$	$K \times 10^3$
0	39.85	..
75.5	33.87	2.12
166.6	27.93	2.13
225.8	24.54	2.15
290.0	21.49	2.14
336.4	19.54	2.12
	Av.	2.13

Experimental Results

Neutral Salt Effect upon Decomposition of Hydrogen Peroxide by Potassium Iodide.—Since aluminum oxyiodide sols in the presence of added electrolyte have velocity constants approaching a value for which the total iodide of the system is unbound, it was thought advisable to investigate the salt effect on H_2O_2–KI systems under conditions comparable with those existing in the work on sols.

Table II shows a list of values for unimolecular velocity constants of a 1.544×10^{-3} N potassium iodide solution in the presence of various salt concentrations.

TABLE II

THE DECOMPOSITION OF HYDROGEN PEROXIDE BY 1.544×10^{-3} N KI IN THE PRESENCE OF POTASSIUM SALTS

Salt concn. equiv./liter	$K \times 10^3$ in presence of			
	Nitrate	Acetate	Sulfate	Tartrate
0	2.15	2.15	2.15	2.15
6.0×10^{-4}	2.16	2.18	2.15	2.14
6.0×10^{-3}	2.15	2.23	2.15	2.19
6.0×10^{-2}	2.17	2.21	2.13	2.19

It can be seen from Table II that the salt effect is less than 4% over the concentration range investigated. Walton[11] observed similar behavior for the cases of potassium nitrate and sulfate. The specific constant of 0.001544 N potassium iodide calculated from the data in Table II is 1.39 $min.^{-1}$ which is in good agreement with Walton's[11] value of 1.35 and with Liebhafsky's[2,12] value of 1.38.

The specific constant increased with dilution; however, when corrections were made for the decomposition of hydrogen peroxide by water, the specific constant remained practically unaltered.

Effect of Salts upon the Decomposition of Hydrogen Peroxide by Sols

Neither pure hydrous aluminum oxide nor an aluminum oxychloride hydrosol (0.254 equivalent of aluminum and 0.006 equivalent of chloride per liter) alone or in the presence of the potassium salts (used in this study) had any effect upon hydrogen peroxide.

Typical results for the effect of the added salts are furnished by sol 4 (Table III) and by sols 6 and 8 (Table IV, Figs. 1 and 2). Ten cc. of salt solution was added to 100 cc. of the sol. Then 5 cc. of hydrogen peroxide solution was added to start the reaction. In the case of sol 6, precipitates were produced upon the addition of 0.05 and 0.1 N sulfate and tartrate. Sol 8 showed precipitation upon the addition of 0.1 N acetate, and 0.01 (and higher) sulfate and tartrate. In all

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(11) Walton, *Z. physik. Chem.*, **47**, 185 (1904).

(12) Liebhafsky and Mohammad, THIS JOURNAL, **55**, 3977 (1933).

instances reported in this paper, however, these precipitates remained uniformly suspended during the measurements. In a few experiments, not cited herein, where the precipitates settled out, analogous results were obtained also. In a separate experiment, dry potassium sulfate was added to sol 6 to render it 0.1 N with respect to the sulfate which completely precipitated the micelles.

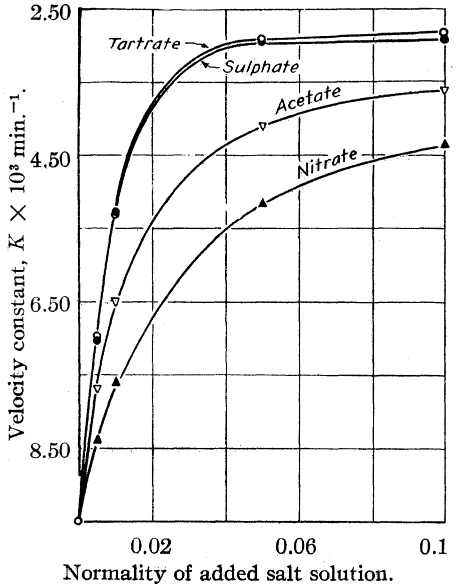

Fig. 1.—Effect of potassium salts on the velocity constant of sol 6. The velocity constant in the case of all iodide unbound is $K = 2.71 \times 10^{-3}$. The normality of salt in the system is found in this and in the remaining figures by dividing "Normality of Added Salt Solutions" by eleven.

After thirty minutes of shaking, the system was centrifuged and the clear supernatant liquid analyzed for iodide. The value of 2.208 milliequivalents per liter was found as compared to 2.234 in the original hydrosol. By a similar procedure the clear supernatant liquid obtained from sol 8 (rendered 8.7×10^{-3} normal with respect to sulfate) showed an iodide content of 1.011 milliequivalents per liter compared to 1.025 in the original sol.

TABLE III

EFFECT OF POTASSIUM SALTS ON VELOCITY CONSTANT[a] OF SOL 4

The velocity constant for the system with all the iodide unbound is 1.91×10^{-3} min.$^{-1}$.

Normality of added salt soln.	Nitrate	Acetate	Sulfate
0.0	7.74	7.74	7.74
.005	7.08	6.54	5.89
.01	5.50	4.89	3.19
.1	4.03	3.13	2.25

[a] Numbers represent $10^3 K$ min.$^{-1}$.

TABLE IV

EFFECT OF POTASSIUM SALTS ON VELOCITY CONSTANT[a] OF SOL 8

The velocity constant for the system in which the total iodide is unbound is 1.24×10^{-3} min.$^{-1}$.

Normality of added salt soln.	Nitrate	Acetate	Sulfate	Tartrate
0.0	3.59	3.59	3.59	3.59
.005	2.95	2.59	2.05	2.13
.01	2.66	2.23	1.38↓	1.40↓
.05	1.81[b]	1.56[b]	1.26↓	1.25↓
.1	1.60[b]	1.41↓	1.27↓	1.25↓

[a] Numbers represent $10^3 K$ min.$^{-1}$. [b] These sols became turbid upon addition of the electrolyte. ↓ Signifies precipitation.

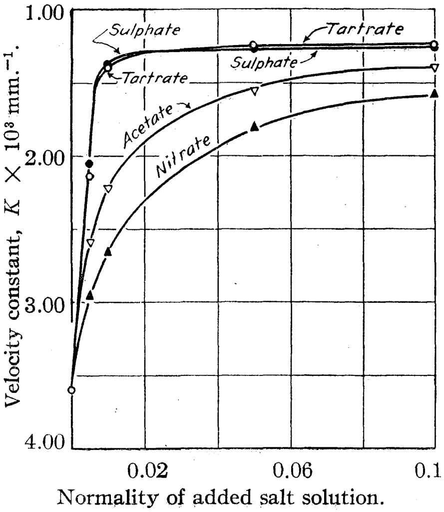

Fig. 2.—Effect of potassium salts on the velocity constant of sol 8.

Since added salts should displace bound iodide from the colloidal particles, it would appear from

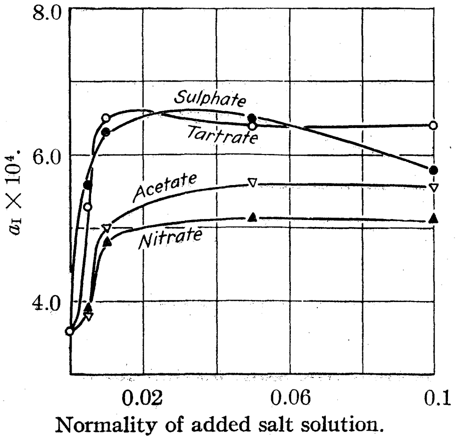

Fig. 3.—Effect of potassium salts on the iodide ion activity of sol 8.

the results of these experiments that the velocity constant for aluminum oxyiodide sols is a measure of the bound iodide of the system. To determine whether the iodide ion activity of the sol increased with addition of salts, silver–silver iodide electrodes were used upon sol 8 with salt concentrations similar to those used in the kinetic experiments. To 20 cc. of sol, 2 cc. of salt solution was added. *p*H measurements were also performed on identical systems. The results are plotted in Figs. 2 and 3.

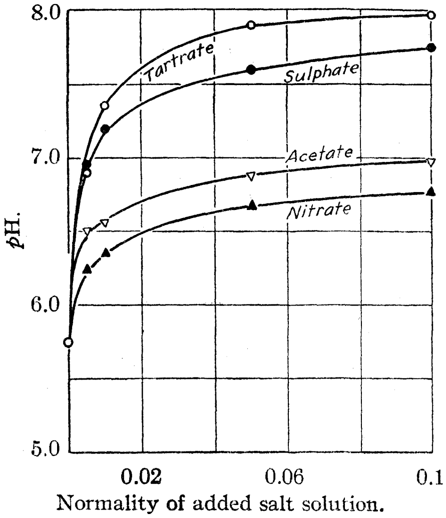

Fig. 4.—Effect of potassium salts on the *p*H of sol 8.

The iodide ion activity measurements were repeated upon sol 7 which was much richer in iodide than sol 8 and not dialyzed. The data obtained are plotted in Fig. 5.

The results obtained with the silver–silver iodide electrode indicate that iodide is being displaced from the colloidal micelles upon the addition of salts. However, it is not possible to estimate the iodide ion concentration in these systems, since the activity coefficients are unknown. The decrease in iodide ion activity at relatively high concentrations for some salts may be due to the decrease in the activity coefficient being larger than the amount of iodide that is displaced. Qualitatively the electrode measurements indicate that the order of effectiveness for potassium salts in increasing the iodide ion activity is about the same as that for decreasing the catalytic activity of these sols. The order of effectiveness of anions in increasing the *p*H of the sols is also the same.

According to the literature concerning the few iodide complexes[13] investigated, the catalytic effect on hydrogen peroxide for these complexes has been less than that for the iodide ion. This research suggests the further investigation of the catalytic effect of iodide complexes.

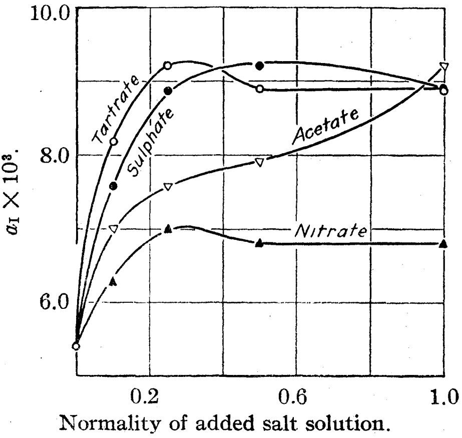

Fig. 5.—Effect of potassium salts on the iodide ion activity of sol 7.

Summary

The catalytic effect of aluminum oxyiodide hydrosols upon the decomposition of hydrogen peroxide is several times greater than that of aqueous solutions of iodide ions of the same concentration: this catalytic activity of these hydrosols is lowered by the addition of certain potassium salts, the order of effectiveness being tartrate > sulfate > acetate > nitrate, this being also the order for their effectiveness in increasing the iodide ion activity of the hydrosols.

It is apparent that basic aluminum micelles containing bound iodide (iodo groups) are more reactive toward hydrogen peroxide than iodide ion and it is postulated that the added anions displace iodo groups from the micelle, converting them to free iodide ions. Iodide ion activity measurements support this postulate and the order of effectiveness is identical to the effectiveness of these anions in replacing hydroxo groups from the micelle, converting them to hydroxyl ions.

NEW YORK, N. Y. RECEIVED OCTOBER 17, 1936

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(13) Walton, *Z. physik. Chem.*, **47**, 185 (1904); Gooding and Walton, *J. Phys. Chem.*, **35**, 3612 (1931).

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

The Heat Capacity of Ethane from 15°K. to the Boiling Point. The Heat of Fusion and the Heat of Vaporization

BY R. K. WITT[1] AND J. D. KEMP

Calorimetric measurements on ethane extending to low temperatures are of interest in the general program of obtaining entropies with the aid of the third law of thermodynamics. The value of the entropy of ethane obtained in this research is also important in demonstrating the correctness of the entropies of other simple hydrocarbons obtained by the application of the third law. This has been discussed briefly by Kemp and Pitzer.[2] A fuller discussion appears concurrently with this paper.

Preparation.—Ethane was prepared by the electrolysis of a potassium acetate solution as suggested by Moser.[3] For purification, the gas was passed successively through a 30% solution of sodium hydroxide, fuming sulfuric acid, concentrated sulfuric acid, an alkaline solution of sodium hydrosulfite, sodium hydroxide sticks and phosphorus pentoxide. Previous to the purification, the line was evacuated with a mercury diffusion pump. About 160 cc. of liquid ethane was prepared and then, for a final purification, fractionated. The middle fraction of 80 cc. was used in the measurements.

The purified ethane contained about 5 parts in a thousand of liquid-soluble, solid-insoluble impurity. This was calculated from the premelting heat effect evident in the heat capacity measurements preceding the melting point.

Apparatus and Measurement of Amount.—The measurements were made with a vacuum calorimeter assembly similar to that described by Giauque and Wiebe.[4] The copper calorimeter used in this research had a volume of 70 cc. A copper–constantan thermocouple, of laboratory designation W-23, was soldered in a well on the bottom of the calorimeter with Wood's metal. W-23 had previously been compared with thermocouple W-22, the present laboratory standard, which had been calibrated directly against a helium thermometer.

The amount of ethane was measured volumetrically in the calibrated bulb described in detail by Giauque and Johnston.[5] The following data from the "I. C. T." were

TABLE I

THE HEAT CAPACITY OF ETHANE

Molecular weight = 30.0462. 1.1391 moles in calorimeter. 0° C. = 273.10° K.

T, °K.	ΔT	C_p, cal./deg./mole	Series
15.53	2.469	0.730	I
21.59	1.928	1.807	I
23.44	1.311	2.139	II
23.59	1.570	2.193	I
26.24	2.216	2.756	I
27.89	2.356	3.096	II
28.78	2.335	3.318	I
30.41	2.119	3.632	II
31.20	2.317	3.915	I
33.00	2.685	4.296	II
33.36	1.901	4.403	I
36.83	4.781	5.239	II
43.15	3.610	6.635	II
46.74	3.024	7.245	II
50.11	2.901	7.828	II
53.29	2.907	8.317	II
56.32	2.543	8.841	II
58.97	2.299	9.28	II
63.03	2.486	9.95	II
66.59	3.891	10.60*	II
70.87	3.975	11.33*	II
75.00	3.491	12.43*	II
78.55	3.090	13.45*	II
81.66	2.710	14.77*	II
84.37	2.365	16.68*	II
86.73	1.901	20.81*	II
89.87	Melting point		
91.59	0.756	16.31	III
92.97	1.645	16.35	III
94.94	1.594	16.33	III
96.60	1.566	16.30	III
98.23	1.498	16.45	III
98.89	1.477	16.33	III
100.49	1.500	16.32	III
104.05	2.504	16.38	III
106.67	2.434	16.45	III
109.24	2.361	16.46	III
111.67	2.308	16.51	III
114.20	2.250	16.48	III
116.24	2.565	16.52	III
119.33	3.308	16.55	III
122.72	3.185	16.58	III
125.96	3.089	16.62	III
129.47	3.587	16.61	III
134.49	4.123	16.63	III
138.72	3.976	16.66	III
142.83	3.845	16.69	III
145.97	3.714	16.73	III
149.80	3.631	16.79	III
153.58	3.519	16.90	III
157.95	4.638	16.90	III
162.82	4.280	16.96	III
167.43	4.430	17.08	III
172.02	4.144	17.09	III
176.54	3.994	17.21	III
180.88	3.891	17.22	III
184.1	Boiling point		

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(1) National Research Fellow, academic years 1931–1933.

(2) Kemp and Pitzer, *J. Chem. Phys.*, **4**, 749 (1936).

(3) Moser, "Die Reindarstellung von Gasen," F. Enke, Stuttgart, 1920.

(4) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

(5) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

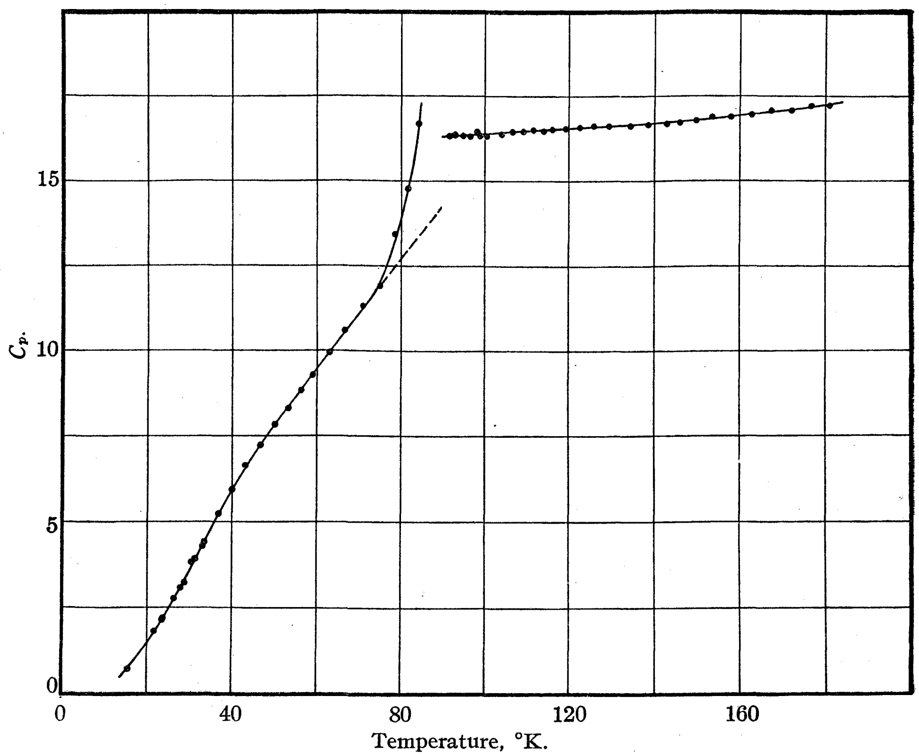

Fig. 1.—Heat capacity of ethane in calories per mole per degree.

used in the calculation: gas density at 0° and 760 mm. = 1.3566 g./l., molecular weight = 30.0462, coefficient of thermal expansion = 0.0036777 and the coefficient of deviation from Boyle's law = −0.00120. The pressure observations were converted to international atmospheres.

The Heat Capacity of Ethane.—The heat capacity measurements were calculated using the method described by Giauque and Johnston.[5] Corrections were made for the heat effects due to the evaporation into the dead space above the liquid in the calorimeter. The constants used for the energy calculation were: 1.0004 absolute joules = 1 international joule, 4.185 absolute joules = 1 calorie.

The heat capacity data are collected in Table I. Fig. 1 gives a graphical representation of the heat capacity measurements.

The heat capacity measurements in Table I which are marked with an asterisk are high due to the premelting effect caused by the presence of impurities in the ethane.

Values of the heat capacity of ethane taken from the smooth curve are given in Table II. Correction has been made in this table for the effect of premelting on the measured heat capacities. The percentage deviations of the results of other observers from those of this research are also given in Table II.

The measurements of Wiebe, Hubbard and Brevoort[6] on liquid ethane are in excellent agreement with our results. The work of Eucken and Hauk,[7] however, shows extremely large deviations. Wiebe, Hubbard and Brevoort[6] have discussed these deviations adequately.

Table II

Heat Capacity of Ethane

Molecular weight, 30.0462. Values taken from smooth curve through observations.

T, °K.	C_p, cal./deg./mole	% deviation W., H. and B. —W. and K.	% deviation E. and H. —W. and K.
15	0.655		
20	1.535		
25	2.470		
30	3.590		
35	4.785		
40	5.944		
50	7.810		
60	9.450		
70	11.09		
80	12.72		
90	16.30		
100	16.38	−0.1	9.9
110	16.47	− .6	9.6
120	16.55	− .7	14.2
130	16.61	− .4	16.2
140	16.69	− .1	17.9
150	16.79	+ .2	19.7
160	19.93	.4	21.7
170	17.08	.8	23.0
180	17.26	.7	24.0

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(6) Wiebe, Hubbard and Brevoort, This Journal, **52**, 611 (1930).

(7) Eucken and Hauk, *Z. physik. Chem.*, **134**, 161 (1928).

The accuracy of our measurements is estimated to be about 0.4% from 35°K. to the boiling point of ethane. At 25°K., the accuracy may be about 1% decreasing to about 2 or 3% at 20°K. and to about 5% at 15°K.

The Melting Point and Boiling Point of Ethane.—The melting point was observed for various percentages of the ethane melted. 89.87 ± 0.1° K. was obtained as the melting point of ethane, after appropriate correction was made for the amount of impurity present.

Only a rough measurement was made of the boiling point. The value obtained was 184.1 ± 0.1°K. Table III summarizes measurements of the melting and boiling points of ethane.

TABLE III

MELTING POINT AND BOILING POINT TEMPERATURES OF ETHANE

(0°C. = 273.10°K.)

M. p., °K.	B. p., °K.	Observer
...	180.1	Olszewski[8] (1894)
100.9	187.7	Ladenburg and Krügel[9] (1900)
...	184.6	Maass and McIntosh[10] (1914)
...	183.8	Burrell and Robertson[11] (1915)
...	184.47	Loomis and Walters[12] (1926)
89.45	...	Wiebe, Hubbard and Brevoort[6] (1930)
89.87 ± 0.1	184.1 ± 0.1	This research

The Heat of Fusion.—The heat of fusion was measured by starting the energy input at a temperature somewhat below the melting point and continuing until a temperature a few degrees above the melting point was reached. Correction was made for the $\int C_p dT$ and the premelting effect. Table IV summarizes the data on the heat of fusion.

TABLE IV

THE HEAT OF FUSION OF ETHANE

Temperature interval	Corrected total heat input per mole	$\int C_p dT$ and premelting effect	ΔH, cal./mole
86.729–91.038	739.6	57.0	682.6
86.776–90.447	727.1	44.1	683.0
86.395–91.696	756.7	73.6	683.1
		Accepted value	682.9 ± 0.7

Wiebe, Hubbard and Brevoort[6] have obtained 667.5 cal./mole for the heat of fusion of ethane. This value is probably low due to their inability to apply an accurate premelting correction. They had a larger amount of impurity and could not extend their measurements to a low enough temperature in order to obtain a reasonably good idea of the course of the true heat capacity of ethane near the melting point.

The Heat of Vaporization.—The heat of vaporization of ethane was measured directly using the five-liter measuring bulb and a constant pressure regulating device described by Giauque and Johnston.[5] Table V gives a summary of the heat of vaporization measurements.

TABLE V

THE HEAT OF VAPORIZATION OF ETHANE

Boiling point 184.1°K. Molecular weight 30.0462

Amount evaporated, mole	Time of energy input, min.	ΔH at 760 mm., cal./mole
0.16816	75	3514
.18853	75	3520
.18443	75	3507
.16350	75	3513
.16382	75	3517
	Mean value	3514 ± 3.5

No other direct measurements of the heat of vaporization have been made. Values of the heat of vaporization obtained from vapor pressure equations cannot be given any weight in comparison to the direct observations.

The Entropy of Ethane.—An itemized account of the entropy of ethane is presented in Table VI. In obtaining the entropy of the solid, the extrapolated heat capacity curve in the neighborhood

TABLE VI

THE ENTROPY OF ETHANE

Molecular weight 30.0462

0–15° K. Debye function $hc\nu/k = 131$	0.24
15–89.87°K., graphical	10.50
Fusion 682.9/89.87	7.60
89.87–184.1°K., graphical	11.95
Vaporization 3514/184.1	19.09
Entropy of actual gas at the boiling point	49.38 ± 0.15 e.u.
Correction for gas imperfection	0.16
Entropy of ideal gas at the boiling point	49.54 e.u.
$\int_{184.1}^{298.1} C_{p(\text{gas})}\, d \ln T$, graphical[13]	5.31
Entropy of ideal gas at 298.1° K.	54.85 ± 0.2 e.u.

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(8) Olszewski, *Berl. Ber.*, **27**, 3305 (1894).

(9) Ladenburg and Krügel, *Ber.*, **33**, 637 (1900).

(10) Maass and McIntosh, THIS JOURNAL, **36**, 737 (1914).

(11) Burrell and Robertson, *ibid.*, **37**, 1893 (1915).

(12) Loomis and Walters, *ibid.*, **48**, 2051 (1926).

(13) This is obtained from the data of Eucken and Parts, *Z. physik. Chem.*, **B20**, 184 (1933).

of the melting point was used, as the heat of fusion has been corrected for the effect of premelting. Thus very little uncertainty is introduced in the calculation of the entropy by the premelting effect.

The expression, $\Delta S = R(27T_c^3P/32T^3P_c)$, obtained by using Berthelot's equation in connection with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, was used to correct the entropy for gas imperfection at the boiling point. The critical pressure and temperature were taken as $P_c = 48.8$ atm and $T_c = 305.2$°K.[14]

The discussion of Kemp and Pitzer in the following paper shows that it is correct to use the third law value of the entropy of ethane in thermodynamic calculations.

Summary

The heat capacity of solid and liquid ethane has been measured from 15°K. to the boiling point.

The melting point of ethane has been determined to be 89.87 ± 0.1°K. The heat of fusion of ethane has been found to be 682.9 cal./mole.

The heat of vaporization of ethane at the boiling point has been found to be 3514 cal./mole.

The entropy of ethane gas at the boiling point calculated from the above data is 49.54 e.u. The entropy at 298.1°K. is 54.85 e.u.

Berkeley, Calif. Received November 16, 1936

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[14] Pickering, *J. Phys. Chem.*, **28**, 97 (1924).

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

The Entropy of Ethane and the Third Law of Thermodynamics. Hindered Rotation of Methyl Groups

By J. D. Kemp and Kenneth S. Pitzer[1]

Since the development of methods of calculating entropy from spectroscopic and molecular structure data, it has become possible to investigate the practical applicability of the third law of thermodynamics in a larger number of cases than previously. For many molecules, there is no question about the correctness of directly applying the third law to low temperature heat capacity measurements in obtaining entropies to be used in thermodynamic calculations. However, in certain cases, false equilibrium, encountered in obtaining low temperature calorimetric measurements, has complicated the use of the third law. The reasons for the complications in the several known cases are understood, and the immediate problem is to gather more information as to which molecules will be affected in order to increase the general usefulness of the third law.

The discrepancy found in hydrogen was first explained correctly by Giauque and Johnston,[2] who suggested the possibility of similar discrepancies in other molecules containing symmetrically placed hydrogens. Later investigations of the entropies of ammonia,[3] hydrogen sulfide[4] and methane[5] have shown that there is no persistence of rotation in the crystal lattices of these molecules which contain symmetrically placed hydrogens. A discrepancy has been found to exist in the case of water, but it has been explained by Pauling[6] as due to the formation of hydrogen bonds in the crystal. In all of these cases, there is no reason to doubt that the calculation of the entropies from molecular structure data is correct.

As attempts are made to deal with larger and more complicated molecules, it becomes more difficult to obtain sufficient molecular data to make even approximately correct calculations of thermodynamic quantities. An increased knowledge as to which molecules the third law may be applied unambiguously will thus be very valuable.

It is of interest therefore to consider the correlation between the third law value of the entropy of ethane obtained by Witt and Kemp[7] and the various possible values of the entropy which may be calculated assuming different molecular models.

In this paper, a comparison of the third law value for the entropy of ethane with one derived

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[1] Shell Research Fellow, academic year 1936–1937.

[2] Giauque and Johnston, This Journal, **50**, 3221 (1928). See also Giauque, *ibid.*, **52**, 4816 (1930).

[3] Overstreet and Giauque, *ibid.*, **59**, 254 (1937).

[4] Giauque and Blue, *ibid.*, **58**, 831 (1936).

[5] Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

[6] Pauling, This Journal, **57**, 2680 (1935).

[7] Witt and Kemp, *ibid.*, **59**, 273 (1937).

from reliable data on the heat and free energy of hydrogenation of ethylene will be found to prove definitely that no false equilibrium exists in ethane. This, of course, means that it is correct to use the third law value in thermodynamic calculations.

In order to make a statistical mechanical calculation of the entropy of ethane, it will be necessary to consider the energy levels of the restricted rotator.

The Energy Levels of Ethane.—Since the spectroscopic interpretation of ethane is uncertain, it was necessary to make certain assumptions with regard to the potential barrier hindering the internal rotation of the methyl groups. A potential function, $^1/_2\, V_0\,(1 - \cos 3\phi)$, which gives three humps of height V_0, was assumed to modify the relative rotation of the methyl groups. Although this form of the potential function is entirely arbitrary, it is a reasonable one and is the only form for which solutions of the wave equation are available.

The quantum mechanical problem as set up in the preceding paragraph has been solved by Nielsen[8] and by Teller and Weigert,[9] who found that the wave equation separates into two parts. One of these is the usual equation for the rotation of a symmetric top with energies

$$W_{J,K} = \left(\frac{h^2}{8\pi^2}\right)\left[\frac{J(J+1)}{I_z} + K^2\left(\frac{1}{I_z} - \frac{1}{I_x}\right)\right]$$

while the second may be transformed easily into Mathieu's differential equation. Of the acceptable solutions for the latter, some are the ordinary Mathieu functions for which the characteristic values and thereby the energies are given by Ince.[10] The energies for the remaining solutions were obtained easily with sufficient accuracy for the present purpose by approximate means.

Nuclear spin was neglected in all calculations, and the molecules were assumed to be equally divided between states with odd and even values of the quantum number K. A symmetry number of 18 was used.

For vibrational frequencies we have used the assignment of Teller and Topley[11] except for one frequency $^2\nu_\alpha^M$ which they fixed only from specific heat data assuming free internal rotation. We have fixed $^2\nu_\alpha^M$ by the same method, obtaining different values depending on the restricting potential, V_0. The order of magnitude has been restricted to about 1000 cm.$^{-1}$ as indicated by the analogous frequencies in ethylene.

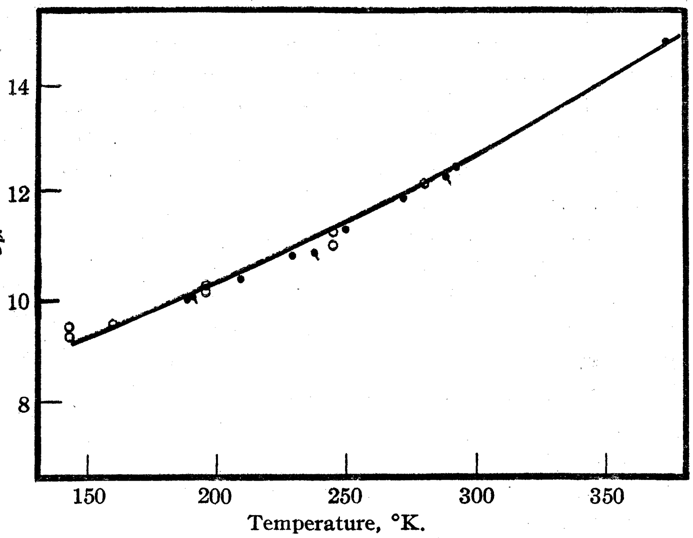

Fig. 1.—Heat capacity of ethane gas in calories per mole per degree: ● Eucken and Parts; ● Heuse; ○ Eucken and Weigert; the smooth curve represents the theoretical calculation.

It has been assumed that each methyl group has the same configuration as in methane and that the carbon–carbon distance is 1.52Å. One thus obtains $I_z = 40.1 \times 10^{-40}$ g. cm.^{2} and $I_{CH_3} = I_x/2 = 5.4 \times 10^{-40}$ g. cm.^{2}.

The Heat Capacity of Ethane Gas.—The heat capacity of ethane gas has been measured recently by Eucken and Parts[12] and by Eucken and Weigert.[13] Their results agree very well with the earlier measurements of Heuse.[14] Eucken and Parts, whose measurements extend down to the boiling point, find that their data may be fitted either by the assumption of free rotation with the unknown frequency $^2\nu_\alpha^M = 712$ cm.$^{-1}$ or with a torsional vibration of frequency 298 cm.$^{-1}$ and $^2\nu_\alpha^M = 920$ cm.$^{-1}$. Eucken and Weigert compared the thermal conductivity of ethane and ethylene and, assuming the same accommodation coefficient for both, calculated the heat capacity for ethane down to 140°K. Using the calculations of Teller and Weigert,[9] they found

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(8) Nielsen, *Phys. Rev.*, **40**, 445 (1932).

(9) Teller and Weigert, *Nachr. Ges. Wiss. Göttingen. Math. physik. Klasse*, 218 (1933).

(10) Ince, *Proc. Roy. Soc. Edinburgh*, **46**, 316 (1925–26).

(11) Teller and Topley, *J. Chem. Soc.*, 876 (1935).

(12) Eucken and Parts, *Z. physik. Chem.*, **B20**, 184 (1933).

(13) Eucken and Weigert, *ibid.*, **B23**, 265 (1933).

(14) Heuse, *Ann. Physik*, **59**, 86 (1919).

that the best fit is obtained with a potential barrier of 315 cal.

We have also calculated the heat capacity of ethane in the range 140 to 400°K. and find that in addition to the combination $V_0 = 315$ cal., ${}^2\nu_\alpha{}^M = 750\ \text{cm.}^{-1}$,[15] a fit may also be obtained for V_0 near 3150 cal. and ${}^2\nu_\alpha{}^M = 1160\ \text{cm.}^{-1}$ as is seen in Fig. 1. The latter is, of course, essentially the second alternative of Eucken and Parts, but is based on a restricted rotator model rather than an oscillator. Since no other reasonable combinations of V_0 and ${}^2\nu_\alpha{}^M$ even approximate the specific heat curve, we need consider only these two in later calculations.

The Entropy of Ethane.—We have calculated the entropy of ethane from molecular structure data using the familiar expression for the rotational entropy of a rigid symmetric top and adding to it the entropy due to the hindered internal rotation of the methyl groups and the ordinary vibrational and translational contributions. A symmetry number of 18 was used.

It has been shown that in order to explain the observed heat capacity of ethane gas, a potential barrier of about 3150 cal. or one near 315 cal. must be assumed. Table I gives a comparison of the entropy of ethane, calculated from molecular structure data, assuming various potential barriers, with the calorimetric entropy obtained by Witt and Kemp.[7]

TABLE I

THE ENTROPY OF ETHANE CALCULATED FROM MOLECULAR STRUCTURE DATA COMPARED WITH THE ENTROPY OBTAINED CALORIMETRICALLY FROM THE THIRD LAW[16]

T, °K.	Potential barrier V_0, cal./mole	Statistical mechanical entropy, cal./deg./mole	Third law entropy, (exptl.) cal./deg./mole
184.1	0	51.09	
184.1	315	50.98	
184.1	3150	49.30	49.54 ± 0.15
298.1	0	56.36	
298.1	315	56.26	
298.1	3150	54.62	54.85 ± 0.2

It may be seen from Table I that there is agreement between the calorimetric and calculated entropies, within the limits of uncertainty, when a potential barrier of 3150 cal. is assumed.

A further comparison may be obtained between the third law entropy and entropies calculated from the heat and free energy of hydrogenation of ethylene. The heat of hydrogenation of ethylene has been measured accurately by Kistiakowsky and co-workers.[17] A preliminary value calculated from heats of combustion by Rossini[18] is in very good agreement with the direct determination of Kistiakowsky. The equilibrium data have been summarized by Teller and Topley[11] and the value they select as the most reliable ($\log K_p = 1.613$ at 863°K.) was used in our calculations. The entropy change in the reaction $C_2H_4 + H_2 = C_2H_6$ may then be obtained at 355°K., provided that the heat capacities of the various gases are known from 355 to 863°K. It is given by the expression

$$\Delta S^\circ_{355} = \frac{\Delta H^\circ_{355} - \Delta F^\circ_{863}}{863} - \int_{355}^{863} \Delta C_p \left(\frac{1}{T} - \frac{1}{863}\right) \mathrm{d}T$$

Since no experimental data are available on the heat capacity of ethane above 400°K., it was necessary to calculate that quantity, using the various molecular models found to give satisfactory heat capacities below 400°K. Fortunately, as can be seen in the expression above, the effect of the heat capacity is small, particularly at the higher temperatures. In calculating the entropy of ethane from the heat and free energy of the hydrogenation of ethylene, the assignment of frequencies of ethylene given by Bonner[19] and the moments of inertia given by Badger[20] were used. The entropy of ethylene at 355°K. obtained by using these values is 54.43 e.u. The thermodynamic constants for hydrogen were taken from the tables given by Davis and Johnston.[21] The values of the entropy of ethane so obtained depend chiefly upon the ΔF and ΔH of hydrogenation of ethylene and only to a small extent upon the assumption made regarding the potential barrier.

Table II gives a comparison between the third law value of the entropy of ethane and the value obtained from the ΔH and ΔF of hydrogenation of ethylene. For further comparison, values of the entropy obtained from a statistical mechanical calculation are also included.

The comparison of the entropies obtained from ΔF and ΔH with the entropy obtained from the third law shows that, regardless of the

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[15] The difference between Teller and Topley's assignment of the remaining vibration frequencies and that of Eucken and co-workers leads to the difference in ${}^2\nu_\alpha{}^M$.

[16] The values in this table differ slightly from the preliminary survey by Kemp and Pitzer, *J. Chem. Phys.*, **4**, 749 (1936).

[17] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935). See also Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **58**, 137 (1936).

[18] Kassel, *J. Chem. Phys.*, **4**, 435 (1936). A personal communication from F. D. Rossini.

[19] Bonner, THIS JOURNAL, **58**, 34 (1936).

[20] Badger, *Phys. Rev.*, **45**, 648 (1934).

[21] Davis and Johnston, THIS JOURNAL, **56**, 1045 (1934).

TABLE II

A SUMMARY OF THE ENTROPY OF ETHANE AT 355°K.

Potential barrier, V_0, cal./mole	0	315	3150
S_{355} from molecular structure data, cal./deg./mole	58.74	58.64	57.06
S_{355} from ΔH°_{355} and ΔF°_{863}, cal./deg./mole (exptl.)	56.61	56.61	57.34
S_{355} from the third law, cal./deg./mole (exptl.)		57.20 ± 0.2	

height of the potential barrier assumed, no residual entropy, such as would be left if there were false equilibrium in the crystal at very low temperatures, remains after the ordinary extrapolation of the heat capacity data to absolute zero. Indeed, for barriers lower than 3150 cal., the impossible situation of obtaining too much entropy from the third law arises. As the correctness of the third law value for the entropy of ethane is now established, the values calculated assuming potential barriers of 315 cal. or less must be in error. It is strong evidence for the existence of a potential barrier of the order of 3000 cal. per mole, which has heretofore been considered improbable.[10,22]

Unfortunately, numerous statistical mechanical calculations have been published with respect to molecules allowing similar rotations for which no potential barrier was assumed. The results for ethane suggest that the entropies so calculated may be in error by as much as 1.5 cal./deg./mole for each internal rotation.[23] Several authors have obtained such disagreements. Kassel[18] was unable to correlate the ΔF and ΔH for the hydrogenation of some higher olefins, finding entropy differences of from 2 to 3 cal./mole/deg. Since one single bond has been formed and the restricting potentials for others probably have been changed by the reaction, the apparent disagreement may well be due to the assumption of completely free rotation in the calculations. Aston and Messerly[24] in the case of tetramethylmethane obtained a disagreement of about 8 cal./deg./mole between the third law entropy and a calculated value of the entropy, while Kassel[25] obtained a similar difference of 3.76 cal./deg./mole for *n*-butane. They suggested that the calorimetric rather than the calculated entropies (assuming free rotation) are in error and ascribe the disagreement to a lack of equilibrium in the crystal at very low temperatures. The work on ethane indicates that this view is probably erroneous and that the entropies of simple hydrocarbons obtained from the application of the third law of thermodynamics to calorimetric data extending to hydrogen temperatures are the correct entropies to use in thermodynamic calculations. As we now know that the calorimetric entropies of ammonia, hydrogen sulfide, methane and ethane are the correct ones to use in thermodynamic calculations, an even more general statement may be made. That is: very probably no molecules other than hydrogen and deuterium retain any entropy due to the persistence of rotation in the crystal below 10°K.

Summary

The entropy of ethane has been calculated from the heat and free energy of hydrogenation of ethylene considering ethane as a restricted internal rotator. A comparison of the values so obtained, with the entropy obtained from calorimetric measurements extending to low temperatures by use of the third law of thermodynamics, proves the correctness of the third law value.

Very strong evidence has been presented for the existence of a potential barrier of about 3150 cal./mole restricting the internal rotation of the methyl groups in ethane by the comparison of the experimental values of the entropy of ethane with values obtained from statistical mechanical calculations. It is believed that the discrepancies noted by some authors in the cases of other hydrocarbons are due to the assumption of incorrect molecular models involving free internal rotation of the methyl groups. From a knowledge of the correctness of the third law entropies in the cases of ammonia, hydrogen sulfide, methane and ethane, it may be stated that very probably no molecules other than deuterium and hydrogen will have any residual entropy due to the persistence of rotation in the crystal at temperatures below 10°K.

BERKELEY, CALIF. RECEIVED NOVEMBER 16, 1936

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[22] (a) Eyring, THIS JOURNAL, **54**, 3191 (1932).

[23] Where six rather than three potential humps would be present it is quite possible that free rotation may be good approximation.

[24] Aston and Messerly, *J. Chem. Phys.*, **4**, 391 (1936).

[25] Kassel, *ibid.*, **4**, 276 (1936).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY DENTAL SCHOOL]

Chloro and Fluoro Compounds Related to Adrenalone

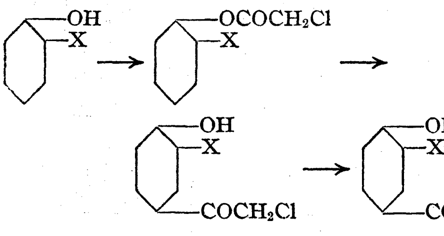
BY HAROLD L. HANSEN

The influence of nuclear chlorine and bromine on the chemical and pharmacological properties of amines of the pressor type has engaged the attention of several investigators. Zeynek[1] prepared both 3,5-dichloro- and 3,5-dibromotyramine. Glynn and Linnell[2] prepared ω-amino-3,4-dichloroacetophenone as well as 3,4-dichlorophenyl-β-aminoethanol and reported for the latter substance a pressor effect much smaller than that of epinephrine but also a correspondingly lower toxicity. While the present investigation was in progress Edkins and Linnell[3] published a report on the preparation of 3-chloro-4-hydroxy-ω-aminoacetophenone and several derivatives of ω-aminoacetophenone bearing nuclear chlorine or bromine.

Aside from the work of Schiemann and Winkelmüller[4] on 3-fluoro-4-hydroxyphenylethylamine and 3-fluorophenylethylamine no reference was found in the literature to pressor compounds containing nuclear fluorine.

The purpose of this investigation was to prepare and to make a preliminary pharmacological study of 3-chloro-4-hydroxy-ω-methylaminoacetophenone and of the corresponding fluorine compound, 3-fluoro-4-hydroxy-ω-methylaminoacetophenone. Both of these are closely related chemically to adrenalone and it was hoped they might be of some value in a study of the comparative influence of chlorine and fluorine on substances of the vaso pressor type.

The synthetic methods employed in this investigation are well known and may be summarized as follows



Various attempts to reduce the amino ketones to the secondary alcohols, including the use of hydrogen with a platinum catalyst, sodium amalgam in acid solution and aluminum amalgam, either failed to give the desired products or produced small amounts of compounds which it has not yet been possible to identify. Apparently both removal of halogen and splitting of the carbon–nitrogen bond were involved in these reduction reactions. Edkins and Linnell[3] were unable to obtain the secondary alcohol from 3-chloro-4-hydroxy-ω-aminoacetophenone by reduction.

The structures of both derivatives of adrenalone reported here were established by conversion of these compounds to the corresponding halogenated methoxybenzoic acids, the constitution and physical properties of which have been previously reported.

Preliminary pharmacological work shows that both 3-fluoro-4-hydroxy-ω-methylaminoacetophenone and the corresponding chloro compound possess vaso pressor properties weaker than that of adrenalone. Intravenous injections into anesthetized dogs produced a blood pressure rise of 2 to 4 mm. of mercury with doses of 1.3 mg./kg. The work also indicates that the fluoro compound is somewhat less active than the chloro.

Experimental Part

***o*-Chlorophenyl Chloroacetate.**—This was prepared from 119 g. of thionyl chloride, 94.5 g. of chloroacetic acid and 128.5 g. of *o*-chlorophenol according to the procedure used by Hartung, Munch, Miller and Crossley[5] in the synthesis of phenyl propionate. The yield of oily product, b. p. 123–125° at 6 mm., was 154 g. or 75%. After two distillations under reduced pressure the product had the following properties: d^{25}_4 1.3589, n^{25}_D 1.5335; *MR*D found 46.86; calcd. 46.33.

Anal. Calcd. for $C_8H_6OCl_2$: Cl, 34.60. Found: Cl, 34.44.

3-Chloro-4-hydroxy-ω-chloroacetophenone.—*o*-Chlorophenyl chloroacetate, 102 g. was dissolved in about 100 cc. of carbon disulfide and treated with 53 g. of anhydrous aluminum chloride according to the directions of Hartung, *et al.*[5] At the end of the reaction the hard black mass was pulverized and added in small portions with brisk stirring to a mixture of concentrated hydrochloric acid and ice. The black precipitate was removed by suction filtration, dissolved in ether and the ether solution dried over sodium sulfate. The solid remaining after removal of the

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(1) Zeynek, *Z. biol. Chem.*, **114**, 275 (1921).

(2) Glynn and Linnell, *Quart. J. Pharm. Pharmacol.*, **5**, 480 (1932).

(3) Edkins and Linnell, *ibid.*, **9**, 75 (1936).

(4) Schiemann and Winkelmüller, *J. prakt. Chem.*, **135**, 101 (1932).

(5) Hartung, Munch, Miller and Crossley, THIS JOURNAL, **53**, 4149 (1931).

TABLE I

ANALYTICAL AND OTHER DATA FOR THE FLUORO COMPOUNDS

Compound	Yield, %	B. p., °C. (4 mm.)	M. p., °C.	Solvent	Formula	Analyses, % Calcd.	Analyses, % Found
o-Fluorophenyl chloroacetate	73	90–94	36–38		$C_8H_6O_2FCl$	Cl, 18.81	18.88
3-Fluoro-4-hydroxy-ω-chloroacetophenone[a]	27–40		101–102	Tol-hept.	$C_8H_6O_2FCl$	Cl, 18.81	18.59
3-Fluoro-4-hydroxy-ω-methylaminoacetophenone[b]	21–31						
3-Fluoro-4-hydroxy-ω-methylaminoacetophenone·HCl	Soft, dark 228°		235–236 dec.	Abs. EtOH	$C_9H_{11}O_2ClFN$	N, 6.38	6.46

[a] Strong irritant and lachrymator. [b] Gray powder, fairly soluble in water.

ether was twice crystallized from dry toluene. The yield varied from 40 to 60 g., or 39 to 59%. Evaporation of the toluene mother liquor gave a few grams of very impure, low melting product which was not studied further. The chloro ketone was further purified by crystallization from dry, crude heptane from which it was obtained as yellow crystals, m. p. 141–142°. This substance is extremely irritating to mucous membrane and is a powerful lachrymator.

Anal. Calcd. for $C_8H_6OCl_2$: Cl, 34.60. Found: Cl, 34.80.

An attempt to prepare this compound by action of phosphorus oxychloride on *o*-chlorophenyl chloroacetate in benzene solution according to the method used by Ott[6] in preparation of adrenalone resulted in failure. The starting material was recovered unchanged.

3-Chloro-4-hydroxy-ω-methylaminoacetophenone.—This compound was prepared according to the directions of Stolz[7] for adrenalone. Fifty grams of finely powdered 3-chloro-4-hydroxy-ω-chloroacetophenone and 25 cc. of absolute ethanol were cooled in an ice–salt bath. To the chloro ketone was added with stirring 100 cc. of a 40% methylamine solution. The reaction mixture was then allowed to stand at room temperature for two days. At the end of this time it was reduced to about one-half its original volume under diminished pressure, thoroughly chilled and filtered by suction. The precipitate was washed with cold water, dissolved in dilute hydrochloric acid and reprecipitated with ammonium hydroxide. The yield of pale yellow crystalline product was about 20 g. or 41%. The hydrochloride of this substance was isolated by evaporation of its aqueous solution on the steam-bath. Crystallization from absolute alcohol gave a faint yellow, water soluble, crystalline material. The substance shrivels at 180°, starts to melt at 210–211° and decomposes at 217°.

Anal. Calcd. for $C_9H_{11}O_2Cl_2N$: N, 5.93. Found: N, 5.99.

Proof of Structure for 3-Chloro-4-hydroxy-ω-methylaminoacetophenone.—The compound obtained above was converted to the methyl ether with methyl sulfate and the resulting ether was oxidized with potassium permanganate. The acid thus obtained was crystallized once from dilute acetic acid, from which it was obtained as small white crystals, m. p. 211–212°. This is in good agreement with the properties listed for 3-chloro-4-methoxybenzoic acid.[8] The benzoic acid derivative obtained above was further converted to the methyl ester which, after one crystallization from dilute ethanol, melted at 94–95°. This corresponds with the properties of methyl 3-chloro-4-methoxybenzoate.[8]

***o*-Fluorophenol.**—This was prepared from *o*-anisidine according to the directions of Schiemann.[9]

Since the procedures employed in the preparation of the fluoro compounds are identical with those previously mentioned, the analytical and other data have been summarized in Table I.

Proof of Structure of 3-Fluoro-4-hydroxy-ω-methylaminoacetophenone.—The phenol was methylated with methyl sulfate and the resulting ether oxidized with potassium permanganate. The acid thus obtained after crystallizing from dilute ethanol melted at 208–210°. 3-Fluoro-4-methoxybenzoic acid[10] has been found to melt at 204°. The 3-fluoro-4-methoxybenzoic acid was further prepared as follows: *p*-cresol was nitrated to produce 3-nitro-4-hydroxytoluene according to the directions of Lucas and Liu.[11] The phenolic compound was converted to the methyl ether with methyl sulfate and the nitro group was reduced to the amine with hydrogen in the presence of a platinum catalyst. The 3-amino-4-methoxytoluene was converted to the fluoro compound which was found to be identical with the 3-fluoro-4-methoxytoluene described by Schiemann.[12] Oxidation with potassium permanganate gave a product with m. p. 208–210°. A mixed melting point determination showed that this substance is identical with the 3-fluoro-4-methoxybenzoic acid obtained from 3-fluoro-4-hydroxy-ω-methylaminoacetophenone.

The pharmacological data presented here were furnished by Professor Carl A. Dragstedt. The author is also grateful for the helpful suggestions of Professor C. M. Suter and Mr. Elmer J. Lawson.

Summary

1. The 3-chloro and the 3-fluoro derivatives of adrenalone have been prepared.

2. Both substances possess weak vaso pressor properties.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 9, 1936

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(6) Ott, *Ber.*, **59**, 1068 (1926).

(7) Stolz, *ibid.*, **37**, 4149 (1904).

(8) Beilstein, 4th ed., Vol. X, p. 176.

(9) Schiemann, *J. prakt. Chem.*, **140**, 97 (1934); **143**, 18 (1935).

(10) Beilstein, 4th ed., Vol. X, p. 175.

(11) Lucas and Liu, THIS JOURNAL, **55**, 1271 (1933).

(12) Schiemann, *Z. physik. Chem.*, **A156**, 415 (1931).

[Contribution from the Chemical Laboratory of The Ohio State University]

A Study of Cellulose Hydrolysis by Means of Ethyl Mercaptan[1]

By M. L. Wolfrom and Louis W. Georges[2]

It is difficult to obtain exact information concerning the structure of the cellulose molecule. The classical methods of organic structural determination involve the study of the breakdown of the organic molecule by degradative methods. The cellulose molecule may be degraded by acid hydrolysis and any new information obtained by a study of this hydrolytic process should be of service eventually in interpreting the true structure of the cellulose molecule. The recent studies of Freudenberg and of Freudenberg and Kuhn[3] on the hydrolytic breakdown of cellulose by sulfuric acid and by acetolysis constitute some of the more important recent contributions to the problem of the constitution of cellulose.

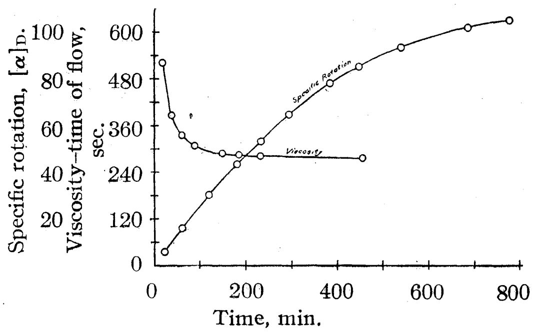

Fig. 1.—Specific rotation and viscosity of 3% solution of cellulose in fuming HCl (d_4^{15} 1.203) at 23°.

In 1913, Willstätter and Zechmeister[4] prepared solutions of cellulose in fuming hydrochloric acid and followed the hydrolysis at 16° by polarimetric and copper reduction methods. With a cellulose preparation that was apparently only solvent-extracted, they obtained an initial induction period and an inflection point at a specific rotation of +14°. In 1923, Sherrard and Froehlke[5] in identifying some purified wood celluloses, demonstrated their similarity to cotton cellulose by applying the polarimetric method of Willstätter and Zechmeister. They also made a run on cotton cellulose as a control. They found the first break in the curve of all celluloses examined at a specific rotation of +43° instead of +14° and found in addition a second break at a specific rotation of +73°. Their temperature of hydrolysis was 20°. It is probable that variations in the type of this polarimetric curve can be ascribed to different methods of cellulose purification.

We have followed polarimetrically the hydrolysis curve at 23° of a sample of chemically purified, high viscosity cotton linters, employing solution concentrations and tube lengths to ensure adequate observed rotations. In agreement with previous work, we find that the initial rotation is zero. With the β-glucose chain conception of the cellulose structure, it is rather difficult to understand why this initial rotation should be zero rather than levo. We did not find any initial induction period, nor did we find any breaks in the curve (Fig. 1). Many intermediate readings other than those shown were obtained. Data were obtained for two concentrations of cellulose and are tabulated in Table I. An analysis of the data (Table I) shows that the calculated monomolecular velocity constants show a slight but definite upward drift. The average value of the velocity constant for the greater part of the reaction is practically independent of the initial cellulose concentration. The polarimetric data so obtained verify the results of Hibbert and Percival,[6] who followed polarimetrically the hydrolysis of cellulose (alkali-purified) in a hydrochloric acid–zinc chloride medium. These workers likewise obtained no breaks in the polarimetric curve and found that the calculated monomolecular velocity constant exhibited a definite upward drift. Their average velocity constant value is in excellent agreement with the one determined in this Laboratory, employing a fuming hydrochloric acid medium at the same temperature.

In agreement with previous workers, we find that the final rotation ($[\alpha]_D$ + 100°) is approximately that of an equivalent amount of d-glucose. The equilibrium rotation of d-glucose is profoundly affected by the hydrogen chloride concen-

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(1) Presented before the Division of Cellulose Chemistry at the 92d Meeting of The American Chemical Society, Pittsburgh, Pennsylvania, September 7, 1936.

(2) Du Pont Cellulose Research Fellow.

(3) K. Freudenberg, "Tannin-Cellulose-Lignin," Verlag J. Springer, Berlin, 1933.

(4) R. Willstätter and L. Zechmeister, *Ber.*, **46**, 2401 (1913).

(5) E. C. Sherrard and A. W. Froehlke, This Journal, **45**, 1729 (1923).

(6) H. Hibbert and E. G. V. Percival, *ibid.*, **52**, 3995 (1930).

tration. This variation is plotted in Fig. 2 and is in fair agreement with previous data. In agreement with Willstätter and Zechmeister,[4] we find that this rotation change is reversible under the conditions of time and temperature employed and accordingly it must represent a true tautomeric shift.

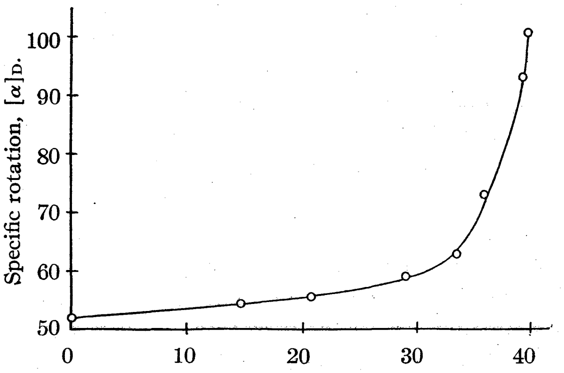

Fig. 2.—Optical rotation of glucose in HCl at 25°.

Table I

Mutarotation of Cellulose in Fuming HCl; Velocity Constant, Temperature 23°

c, 1.004; l, 4-dm.				c, 2.857; l, 4-dm.			
t^a (min.)	α_D deg.	$[\alpha]_D$ deg.	k^b	t^a (min.)	α_D deg.	$[\alpha]_D$ deg.	k^b
19	+0.16	+4.0	0.0021	26	+0.65	+5.7	0.0022
24	.19	4.7	.0020	36	0.98	8.6	.0024
44	.41	10.2	.0024	51	1.36	11.9	.0024
79	.76	18.9	.0026	81	2.22	19.4	.0025
119	1.20	29.9	.0030	101	2.80	24.5	.0026
149	1.49	37.1	.0031	126	3.48	30.4	.0027
179	1.80	44.8	.0033	156	4.26	37.3	.0028
199	1.97	49.1	.0034	186	5.02	43.9	.0029
220	2.08	51.8	.0033	216	5.60	49.0	.0029
259	2.42	60.3	.0036	247	6.40	56.0	.0031
286	2.60	64.7	.0036	297	7.38	64.6	.0032
334	2.88	71.7	.0038	339	8.15	71.3	.0034
391	3.17	78.9	.0040	454	9.77	85.5	.0037
476	3.49	86.9	.0043	544	10.66	93.3	.0041
626	3.85	95.9	.0051	694	11.54	100.9	.0048
∞		100.1		∞		104.6	

[a] The initial time was determined here by the backward extrapolation of the curve to zero rotation. [b] $k = \frac{1}{t} \ln_e \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$ (t in minutes; $\alpha_0 = 0$).

We were also interested in following the viscosity changes in the cellulose solutions. We found that at 25° the first measurable viscosity value was quite low and that the solutions attained the viscosity of an apparent equivalent amount of *d*-glucose when the specific rotation was approximately +25°. These data are shown in Figs. 1 and 3.

The main object of our investigation was to insert a carbonyl reagent into the hydrolytic mixture in order to follow the breakdown of the cellulose molecule by means of the intermediate reaction products. Ethyl mercaptan is a suitable reagent for this purpose. This substance will react with the free reducing groups of sugars in concentrated hydrochloric acid to form the sugar mercaptals or thioacetals.[7] At the present stage of our investigations, the mercaptalated cellulose hydrolytic products, other than glucose ethyl mercaptal, were isolated as amorphous mixtures and no attempt was made to separate them into their pure components. They were characterized by means of their sulfur content.

The reaction between a reducing sugar and ethyl mercaptan takes place with extreme rapidity and at low temperatures. Under the Willstätter–Zechmeister hydrolytic conditions, the effective sugar concentration is relatively low and we found it necessary to study the mercaptalation of *d*-glucose under such conditions. A 5% solution of *d*-glucose in fuming hydrochloric acid can be mercaptalated by vigorous mechanical shaking with an excess of ethyl mercaptan for fifteen minutes at 0°. At the end of this period the solution has lost its Fehling reduction capacity and the glucose diethyl mercaptal may be isolated in approximately eighty per cent yield.

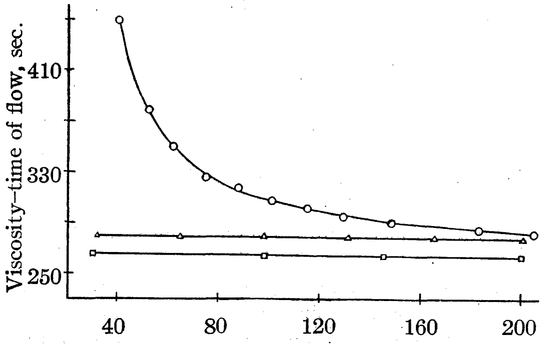

Fig. 3.—Comparison of viscosity at 25°: ○, 3% solution of cellulose in fuming HCl; △, 3% solution of glucose in fuming HCl; □, fuming HCl.

The glucose mercaptal that separates, after sodium bicarbonate neutralization, is contaminated with appreciable amounts of sodium chloride. For quantitative purposes, it was found desirable to leave this salt in the product and correct for its presence by an ash determination. We are probably dealing here with an addition compound

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(7) E. Fischer, *Ber.*, **27**, 673 (1894).

similar in nature to the well-known *d*-glucose–sodium chloride compound. The mother liquor could then be investigated by concentration to dryness and acetylation, the acetylated product being purified by pouring into a large volume of water. Difficulties were here encountered in acetylating quantitatively, a small amount of material adhering to a relatively large amount of crystalline salt that was insoluble in the acetylating mixture.

The optimum mercaptalation procedure thus established for *d*-glucose was then applied to the cellulose hydrolytic solutions and the course of hydrolysis of cellulose (5%) in fuming hydrochloric acid solutions at 16° was studied by means of the mercaptalated products obtained from the reaction of ethyl mercaptan with the cellulose solutions at various stages of hydrolysis. Simultaneous polarimetric data were obtained. Sulfur analyses served to determine the average molecular size of the mixtures of mercaptalated products isolated from the cellulose hydrolysis. The pertinent data are tabulated in Table II. An analysis of these data is given in Table III and shows that the cellulose molecule fragments with extreme rapidity under these conditions. Glucose ethyl mercaptal first appears when the hydrolysis is approximately two-thirds completed. Its amount gradually increases. When the hydrolysis was approximately at the half-period, the

TABLE II

MERCAPTALATED PRODUCTS ISOLATED FROM CELLULOSE SOLUTIONS (*c*, 4.669) IN FUMING HYDROCHLORIC ACID (d^{15}_4 1.203) AT 16°

			Water-insoluble mercaptalated products (from 2.80 g. cellulose)			Acetylated water-soluble products		
Expt.	Time of hydrolysis	$[\alpha]^{16}_D$	% NaCl	Wt. (NaCl-free basis), g.	% S (NaCl-free basis)	Expt.	Wt.	S, %
a	17 min.	..	19.4	2.7	0.33	*a′*	Trace	
b	3 hrs.	+17.5°	0.5	1.5	2.03	*b′*	1.1	4.6
c	6	36.7	0.6	0.7	2.39	*c′*	1.8	6.7
d	9	46.6				*d′*	3.5	7.4
e	12	61.0				*e′*	1.6	6.0
f	15	70.1	0	0.4		*f′*	2.9	6.2
g	18	79.8	5.8	1.1	21.3	*g′*	2.2	6.0
h	21	..	6.4	1.7	21.1	*h′*	1.4	5.7
i	24	91.5	9.5	1.8	21.9	*i′*	2.7	7.1
j	27.5	99.8	17.9	2.1	21.6	*j′*	2.3	6.8
k	34.5	103.0	18.8	2.5	21.1	*k′*	1.2	7.7
l	38.7	104.9				*l′*		
m	51.7	..	11.4	2.5	21.4	*m′*	1.3	6.2
n	55.0	..	20.9	2.4	21.7	*n′*	1.3	6.7

(*a*) The addition of 5 cc. of water preceding the mercaptan addition was omitted.

(*d* to *n*) The acid solution was poured into a suspension of 68 g. of sodium bicarbonate in 100 cc. of water.

(*d*, *e*) No product precipitated.

(*f*) After standing for one day, 0.4 g. of a crystalline product separated. This material was characterized as *d*-glucose diethyl mercaptal. On recrystallization the substance melted at 127° (unchanged on admixture with an authentic specimen of *d*-glucose diethyl mercaptal).

(*g to n*) Crystalline products were obtained which were mixtures of glucose diethyl mercaptal and sodium chloride. They were removed by filtration and were not washed. The sodium chloride content was determined by conversion to sodium sulfate in a platinum crucible with concentrated sulfuric acid. Calcd. for *d*-glucose ethyl mercaptal: S, 22.4. The glucose ethyl mercaptal was isolated and identified as its pentaacetate for one typical run. A portion (1.5 g.) of the crude water-insoluble product from (*k*) was acetylated overnight with acetic anhydride (10 cc.) and pyridine (5 cc.) and poured into ice and water (400 cc.); yield, 1.6 g. On recrystallization from methanol–water the substance was identified as *d*-glucose diethyl mercaptal pentaacetate; m. p. 45–47° (mixed m. p. unchanged); $[\alpha]^{24}_D$ +13.3° (*c*, 3.6; $CHCl_3$).

(*j* to *n*) A second solution of cellulose (30 g.) was prepared as previously described and used after it had been allowed to hydrolyze at 16° for twenty-seven and one-half hours.

(*a′*) A trace of amorphous material was obtained.

(*b′*) A solid, amorphous product was obtained.

(*c′*, *d′*) These products separated as gummy masses contaminated with salt. They were taken up in chloroform and the extract washed with sulfuric acid (1 molar), aqueous sodium bicarbonate and water. On solvent removal and trituration with ether the products were obtained as granular solids.

(*e′* to *h′*) The products separated as viscous sirups which hardened to a solid mass on standing.

(*i′* to *n′*) These sirupy products were treated as described for (*c′*) and (*d′*) and were obtained as glassy solids after drying in a vacuum desiccator.

isolated mixtures of products corresponded to the trisaccharide stage. The amount of this type of material gradually decreased but appreciable quantities were still present at the last point determined.

TABLE III

MOLECULAR SIZE OF ISOLATED MERCAPTAL PRODUCTS

5% Cellulose in fuming hydrochloric acid; temp., 16°. Each experiment equivalent to 2.80 g. cellulose.

Expt.	Time of hydrolysis, hours	$[\alpha]^{16}D$	Water-insoluble product Amount, g.	D. p.[a]	Water-soluble product as acetate Amount, g.	D. p.[a]
a	1/4	..	2.7	121	...	...
b	3	+17.5°	1.5	20	1.1	4
c	6	36.7	0.7	17	1.8	2.5
d	9	46.6	0	.	3.5	2.5
e	12	61.0	0	.	1.6	3
f	15	70.1	0.4	1	2.9	3
g	18	79.8	1.1	1	2.2	3
h	21	..	1.7	1	1.4	3
i	24	91.5	1.8	1	2.7	2.5
j	27.5	99.8	2.1	1	2.3	2.5
k	34.5	103.0	2.5	1	1.2	2
m	51.7	..	2.5	1	1.3	3
n	55	..	2.4	1	1.3	2.5

[a] D. p. = degree of polymerization or number of glucose units in the chain. For (a), (b) and (c), this was calculated by the following close approximation: d. p. = $\frac{100 \times 2S}{\%S \times C_6H_{10}O_5} = \frac{40}{\%S}$.

Further work is in progress in this Laboratory.

Experimental

Cellulose Characterization.—The cellulose used throughout this research was a sample of purified cotton linters[8] of high viscosity which had been subjected to the customary alkali kier and mild bleaching process. The material showed the following characterization: alpha cellulose, 99.2%; ash, 0.04%; iron, 10 p. p. m.; moisture, 4.0%. The material was analyzed for pectin by the Link[9] modification of the Lefèvre–Tollens[10] procedure and was found to be pectin-free by this method. The cuprammonium viscosity of the cellulose was determined in 0.1% concentration at 25 ± 0.02°: $n = 2.732$ centipoises; $[\eta]$ (intrinsic

$$\text{viscosity}) = \frac{\ln_e \eta_r}{C} = \frac{\ln_e \frac{409.5}{192.3}}{0.1} = 7.559.^{11}$$

Preparation and Measurement of Cellulose Solutions.—Fuming hydrochloric acid (98.74 cc.; $d^{15}{}_4$ 1.203) was added to the cotton linters (1.000 g.; moisture content, 4.0%) in a glass-stoppered flask and the mixture shaken until the cellulose was completely dissolved (eight minutes) with occasional cooling in an ice-bath. The density of the solution after three hours of standing was found to be 1.2003; 25°/4°. This made a 1% solution of cellulose (moisture-free basis) in fuming hydrochloric acid. A portion of the solution was used for the polarimetric observations and another portion was used for the direct determination of viscosity in an Ostwald type viscometer. A similar procedure was used in obtaining data for a 3% cellulose concentration. The results obtained for one typical cellulose concentration are shown in Fig. 1. The data shown in Fig. 3 were obtained for comparative purposes. The calculated velocity constant data are tabulated in Table I. The optical rotations of *d*-glucose in various concentrations of hydrochloric acid are shown in Fig. 2.

Reversibility of the Optical Rotation of *d*-Glucose in Concentrated Hydrochloric Acid.—The experiment to be described was performed to determine whether the rotation of *d*-glucose in fuming hydrochloric acid was due to a permanent change in structure or to a reversible tautomeric equilibrium. *d*-Glucose (1.0623 g.) was dissolved in fuming hydrochloric acid ($d^{15}{}_4$ 1.202) to make 50.00 cc. of solution; $[\alpha]_D$ +100.3°. This solution was then diluted to 99.90 cc. with water. This lowered the hydrogen chloride percentage to approximately 20.1% and the concentration of *d*-glucose from *c*, 2.125 to *c*, 1.063; $[\alpha]_D$ +57°. The specific rotation for *d*-glucose in acid of the same concentration was found to be +56°. This indicates that the equilibrium is essentially reversible and that the rotation changes are measures of true tautomeric shifts.

Mercaptalation of a 5% *d*-Glucose Solution.—*d*-Glucose (3.3 g.) was dissolved in 60 cc. of hydrochloric acid ($d^{20}{}_4$ 1.184) and the solution cooled to 0°. Purified ethyl mercaptan (8 cc.; cooled to 0°) was added and the mixture vigorously shaken by mechanical means for fifteen minutes at 0°. The faint yellow solution was poured with stirring into a suspension of 60 g. of sodium bicarbonate in 100 cc. of water. The heat change was negative and the neutralization could thus be effected at low temperatures. The mixture was cooled in an ice–salt bath and the crystalline product removed by filtration, washing being omitted; yield, 4.9 g. or 4.0 g. on a salt-free basis (77%).

Anal. Ash as Na_2SO_4: 21.0. Calcd. as NaCl, 17.3. S (NaCl-free basis): 21.6. Calcd. for $C_6H_{12}O_5(SC_2H_5)_2$, 22.4.

A portion (1.5 g.) of the above salt-containing product was acetylated overnight with acetic anhydride (10 cc.) and pyridine (5 cc.) and poured into 400 cc. of ice and water. A crystalline product was obtained that was characterized as glucose diethyl mercaptal pentaacetate by its melting point of 45–47° (mixed m. p. unchanged); $[\alpha]^{24}D$ +12.8° (*c*, 3.6; $CHCl_3$); yield, 2.1 g. (calcd., 2.17 g.). Wolfrom[12] recorded for this substance the constants: m. p. 45–47°; $[\alpha]^{29}D$ +11° ($CHCl_3$).

Mercaptalation of Cellulose Hydrolytic Products.—An amount of 30 g. of cellulose was dissolved in 600 cc. of fuming hydrochloric acid ($d^{15}{}_4$ 1.203) by shaking in a 1-liter glass-stoppered bottle. After seventeen minutes a clear solution ($d^{15}{}_4$ 1.219) was obtained that contained 4.669 g. of cellulose per 100 cc. of solution. This solution was kept in a thermostated constant temperature bath held at 16 ± 0.1°. The water in the bath was cooled by means of an immersed coil which was connected with a

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(8) Furnished through the courtesy of the Hercules Powder Co., Hopewell, Va.

(9) A. D. Dickson, H. Otterson and K. P. Link, THIS JOURNAL, **52**, 775 (1930).

(10) K. U. Lefèvre and B. Tollens, *Ber.*, **40**, 4513 (1907).

(11) E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 157 (1935).

(12) M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

refrigeration unit. Samples of the solution under investigation were removed at stated intervals for mercaptalation. Polarimetric readings at 16° were taken simultaneously and when plotted showed again a continuous curve. The mercaptalation products were isolated and analyzed. In the experiments herein reported, no attempts were made to isolate the various mercaptalated oligosaccharides in pure form. The data are tabulated in Table II. The various mercaptalations are denoted by letter in this table and will be referred to by these designations. The mercaptalation procedure employed was that described for *d*-glucose, unless otherwise specified. An amount of 60 cc. (equivalent to 2.80 g. of cellulose) of the solution was transferred to a glass-stoppered pressure bottle, 5 cc. of water and 8 cc. of purified ethyl mercaptan were added and the whole shaken mechanically for fifteen minutes at 0°. The addition of a small amount of water at this point lowered the acid concentration to that of ordinary concentrated hydrochloric acid. The product was precipitated by pouring the solution gradually into a suspension of 68 g. of sodium bicarbonate in 200 cc. of water. The excess bicarbonate was neutralized with acetic acid. The material was centrifuged and the residue washed successively with water, ethanol, acetone and petroleum ether. The washed product was dried in a vacuum oven at 50°.

The mother liquors from the precipitates were tested with Fehling's solution and negative results were obtained in each case. They were then concentrated at 55°, under reduced pressure to a moist salt and this transferred to a Büchner funnel, washed with acetone and dried at 40°. The salt residue was then acetylated for two days at room temperature (occasional shaking) with acetic anhydride (36 cc.), and pyridine (18 cc.) and the acetylation product isolated by pouring into ice and water (800 cc.). The data obtained are tabulated in Table II.

The data tabulated in Table II were calculated to their average degrees of polymerization by means of the sulfur analyses and these calculated results are shown in Table III.

The authors are indebted to E. I. du Pont de Nemours and Co., Inc., for the fellowship grant which has made this research possible, and to Dr. Robert W. Rothrock for practical assistance in the experimental work.

Summary

1. Ethyl mercaptan has been used as a reagent to follow the course of hydrolysis of the cellulose molecule in fuming hydrochloric acid.

2. The hydrolysis of cellulose (chemically purified linters of high viscosity) in fuming hydrochloric acid at 23° was followed polarimetrically and by viscosity measurements. The rate of increase of the optical rotation from 0° to that of *d*-glucose ($[\alpha]_D + 100°$) was found to be a continuous function. The calculated monomolecular velocity constants showed a slight but definite upward drift. At an early stage ($[\alpha]_D + 25°$, approx.) of the hydrolysis the viscosity of the solution approached that of a solution containing an equivalent amount of apparent *d*-glucose.

3. The course of hydrolysis of cellulose in fuming hydrochloric acid solutions (5%) at 16° was studied by means of the mercaptalated products obtained from the reaction of ethyl mercaptan with the cellulose solutions at various stages of hydrolysis. Simultaneous polarimetric data were obtained. Control experiments were made to determine the optimum procedure for the mercaptalation of *d*-glucose and this procedure was used in the cellulose reactions. Sulfur analyses served to determine the average molecular size of the mixtures of mercaptalated products isolated from the cellulose hydrolysis.

4. The data indicate a rapid hydrolysis to surprisingly small units. When the hydrolysis was approximately at the half-period, the isolated products corresponded to the trisaccharide stage. Glucose diethyl mercaptal first appeared when the hydrolysis was approximately two-thirds completed and gradually increased in amount.

Columbus, Ohio Received October 6, 1936

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Some New Sulfonic Acid Esters

BY STEWART E. HAZLET[1]

In the course of some other work in progress in this Laboratory it was necessary to prepare some benzene- and *p*-toluenesulfonic acid esters which had not been reported previously. In each case the three isomers have been characterized and the results are summarized in Table I and Table II.

TABLE I

ESTERS OF BENZENESULFONIC ACID

Starting material	Solvent	Crystal form	Yield, %	M. p., °C.	Formula	Analyses, % Halogen Calcd.	Halogen Found	Sulfur Calcd.	Sulfur Found
o-Bromophenol	Methanol	Colorless platelets	90	54–56	$C_{12}H_9O_3BrS$	25.55	25.53[a]		
m-Bromophenol	(B. p. 217–218° at 10.5 mm.)		61		$C_{12}H_9O_3BrS$	25.55	25.78[a]		
p-Bromophenol	Petroleum ether[c]	Colorless needles	67	50–55[d]	$C_{12}H_9O_3BrS$	25.55	25.43[a]		
o-Phenylphenol	Dilute alcohol	Colorless needles	93	66–68	$C_{18}H_{14}O_3S$			10.32	10.34[a]
m-Phenylphenol	(B. p. 273° at 16 mm.)	Colorless solid	94	.....	$C_{18}H_{14}O_3S$			10.32	10.63[b]
p-Phenylphenol	Methanol[e]	Colorless needles	66	104–105	$C_{18}H_{14}O_3S$			10.32	10.63[a]

[a] Determinations made by the Carius method. [b] Determination made by the Parr bomb method. [c] Separated at about −82°. [d] The crude product boiled at 197–206° at a pressure of 2.5 mm [e] Final recrystallizations were from dilute ethyl alcohol.

TABLE II

ESTERS OF *p*-TOLUENESULFONIC ACID

Starting material	Solvent	Crystal form	Yield, %	M. p., °C.	Formula	Analyses, %[a] Halogen Calcd.	Halogen Found	Sulfur Calcd.	Sulfur Found
o-Bromophenol	Dil. alcohol	Colorless plates	98	77–79	$C_{13}H_{11}O_3BrS$	24.46	23.96		
m-Bromophenol	Methanol	Colorless rods	86	52–54	$C_{13}H_{11}O_3BrS$	24.46	24.46		
p-Bromophenol	Dil. alcohol	Colorless rectangular prisms	Quant.	93–95	$C_{13}H_{11}O_3BrS$	24.46	24.35		
o-Phenylphenol	Dil. alcohol; ligroin (68–70°)	Colorless needles	Quant.	64–66	$C_{19}H_{16}O_3S$			9.88	9.94
m-Phenylphenol	Methanol	Colorless cubes	90	52–54	$C_{19}H_{16}O_3S$			9.88	9.88
p-Phenylphenol	Alcohol:acetone = 1:1; benzene–ligroin (68–70°)	Colorless plates	75	178.5–179.5	$C_{19}H_{16}O_3S$			9.88	[b]

[a] These analyses were made by the Parr bomb method. [b] This compound was reported by Bell and Kenyon [*J. Chem. Soc.*, 3049 (1926)]. No yield was recorded; the reported m. p. was 177° for lustrous plates obtained from acetic acid.

To obtain these products the required acid chloride (1.1 mols) was added slowly with agitation to a pyridine solution of the phenol that was held at about 10°. Next the mixture was heated for half an hour at 60°, then gently refluxed for an equal period, cooled and treated with water and dilute hydrochloric acid. Products which separated as solids were collected by filtration; others were extracted with ether. The extracts were shaken successively with a 5% solution of potassium hydroxide, water, 5% hydrochloric acid and water. The ethereal solutions were dried with anhydrous sodium sulfate in the presence of norite. The mixtures were filtered, the ether distilled off, and the products allowed to solidify. The products obtained by either method were purified by crystallization from suitable solvents.

Summary

Some new esters of benzene- and *p*-toluenesulfonic acid have been prepared and their properties reported.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

Organic Oxidation Equivalent Analysis. I. Theory and Applications

BY ROGER J. WILLIAMS

In connection with the problem of analysis of very small samples of biological materials, the possible importance of being able to determine the amount of oxygen required for their complete combustion was noted. Further study revealed the fact that in the case of the vast majority of pure compounds this determination offers an alternative to the familiar "combustions" for carbon and hydrogen.

A search of the literature shows that apparently no one has approached the subject from exactly this angle. Strebinger,[1] using potassium iodate as the oxidizing agent, determined the oxygen required for the complete combustion of organic compounds and from this and the known carbon and hydrogen contents he calculated the oxygen contents of the compounds. Simon and Guillaumin[2] oxidized certain (non-nitrogenous) organic compounds with sulfuric acid and silver dichromate and from the carbon dioxide formed and the oxidizing agent used up calculated the hydrogen content of the compounds. Stanek and Nemes[3] developed a complicated micro method (using iodate) for the quantitative determination not only of the "oxygen consumed" but also carbon, nitrogen and halogens. The determination of oxygen consumed along with the other values made possible with rather complicated equations the calculation of hydrogen content. They pointed out that the amount of oxygen required for complete oxidation of an organic compound is itself a very characteristic quantity, but did not deal experimentally with this determination except as a part of their general set-up for complete micro analysis.

Sample Calculation.—The way in which the oxidation equivalent value may be used as a substitute for "combustion" data in determining the formula for a compound may best be illustrated by a specific case in which we will use the following designations

$C_xH_yO_z$ = formula of unknown
M = its molecular weight
E = its oxidation equivalent (grams oxidized by one gram atom of oxygen; 17.90 in the case cited below)
$M/E = N$ = the number of atoms of oxygen required to oxidize one molecule of the compound.

Suppose that one gram of an "unknown" containing only carbon, hydrogen and oxygen (gluconic acid) is found experimentally to require 0.894 g. of oxygen (calcd. 0.898) for complete combustion. From this it can be calculated that one gram atom of oxygen will completely oxidize 17.90 g. (17.82 calcd.) of the unknown.

The molecular weight M must be an even integer (except in the case of odd molecules) and a multiple of E. Which multiple of E it is, can be determined cryoscopically or better yet, in this case, by titration. If $N = 10$, $M = 178$; if $N = 11$, $M = 196$; if $N = 12$, $M = 214$. Experimentally it is easily ascertained that N is 11.

Of the above values x, y, z, M and N are all integers (of these y and M are *even* numbers) and it is possible to set up the simple Diophantine equations (1) and (2) from which may be derived (3), (3a) and (4).

$$12x + y + 16z = M \qquad (1)$$
$$2x + 0.5y - z = N \qquad (2)$$
$$y = (6N - M + 22z)/2 \qquad (3)$$
$$z = (M - 6N + 2y)/22 \qquad (3a)$$
$$x = (M - 2N - 18z)/8 \qquad (4)$$

Substituting 196 and 11 for M and N, respectively, in equations (3) and (4) we obtain (5) and (6)

$$y = (-130 + 22z)/2 \qquad (5)$$
$$x = (174 - 18z)/8 \qquad (6)$$

Below are given the values of y and x derived from equations (5) and (6) by substituting various integral values of z. From these it is evident that the formula of the unknown can be nothing other than $C_6H_{12}O_7$.

Integral values of z	Corresponding values of y	Corresponding values of x
5	−10	10.5
6	1	8.25
7	12	6
8	23	3.75
9	34	1.5

Calculations for N and S Compounds.—In order to calculate in a similar way the formula for a compound containing reduced nitrogen, $C_xH_yO_zN_b$, M is used to represent the weight of the residue after b equivalents of NH_3 have been subtracted. For calculating in case of a compound contain-

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(1) Strebinger, *Z. anal. Chem.*, **58**, 97–114 (1919).
(2) Simon and Guillaumin, *Compt. rend.*, **176**, 1065 (1923).
(3) Stanek and Nemes, *Z. anal. Chem.*, **95**, 244 (1933).

ing nitrogen and sulfur (both in reduced condition), $C_xH_yO_zN_bS_c$, M is used to represent the residue after $3c$ moles of water have been *added* and b molecules of NH_3 and c molecules of SO_3 subtracted. This is on the assumption that ammonium and sulfate ions are the end products of the oxidation, respectively. Separate analyses for nitrogen and sulfur must, of course, be made.

Applicability to Different Types.—The question naturally arises as to whether the value of the molecular weight of an unknown can be determined with sufficient accuracy so as to make the calculation valid. This problem has been given careful study and there appears to be no difficulty except in the case of certain compounds of carbon, hydrogen and oxygen which have a high molecular weight and/or low value of E, and the molecular weights of which it is impossible to determine by titration or otherwise, with reasonable accuracy. These, however, can be handled as indicated below. In the case of many simpler compounds such as glycerol or oxalic, tartaric and succinic acids the molecular weight determinations as well as those of the oxidation equivalents can be very inexact and yet lead inevitably to the correct results. Nitrogen compounds in general offer no difficulty provided the nitrogen can be determined accurately since the value obtained along with the oxidation equivalent data, is basis for a sufficiently accurate value for the molecular weight. If, in the case of carbon–hydrogen–oxygen compounds which offer difficulty because of uncertainty regarding the molecular weight, one additional fact is known, namely, the degree of unsaturation, then the difficulty disappears. These are illustrated by the type $C_8H_{10}O_4$ and $C_9H_8O_4$, which, in this case, have exactly the same oxidation equivalent value, and molecular weights which differ from each other by less than 6%. They differ markedly in the number of double bonds and/or rings present, however, and could in general be easily differentiated, without a carbon and hydrogen analysis.

With regard to compounds of high molecular weight, calculation of the molecular formula has limitations in accuracy similar to those which hold for traditional combustion analyses. In either case unless the analyses are very accurate, the data may fit several formulas equally well.

Notes on Calculations.—There are several points regarding the calculations which need to be clarified. It is not infrequent that more than one *mathematical* solution to the equations can be found, but that only one falls within the limits possible for a chemical formula. Thus, the same data fit approximately the formulas $C_8H_2O_6$, $C_6H_{12}O_7$ and $C_4H_{22}O_8$, but this should not cause any uncertainty, because the two extremes are either impossible as compounds or else would have very unusual properties. In the case of higher molecular weight compounds two solutions may arise as above, both of which represent *possible* compounds. In such cases the two are so far apart in their hydrogen content that they could be distinguished easily without analysis because of differences in chemical behavior.

It should be emphasized that in order to have a valid calculation, the value of N (which is an integer) *must be correctly assigned.* If this is done, then the value of M is obtained with considerable accuracy ($N \times E$) and by substituting reasonable values[4] of y in equation (3a), z can be established with certainty. These values of z, if substituted in (3) and (4) then lead to integral values of x and y unless the molecular weight value is slightly in error. If it is high or low by two integers the value of x will differ from an integer by $^1/_4$, and y will be an odd number. If M is high or low by 4 integers (but this should not happen if the oxidation equivalent value is obtained with satisfactory accuracy) then the value of x will differ from an integer by $^1/_2$ and y will be even.

Use in Checking Composition.—In practical experience there is seldom an occasion to analyze an organic compound which is entirely unknown. Usually the analysis serves as a check to avoid false assumptions.

Here the usefulness of the oxidation equivalent analysis is apparent when the data in the case are studied. In order to study this problem a table was prepared giving the calculated oxidation equivalent values for all of the C_8 and C_9 compounds (containing C, H, O and reduced N) which are listed in Richter's "Handlexicon." The total number of molecular formulas in the sample was 547 and should be representative.

The oxidation equivalent values in the sample ranged from 4.56 to 99, and it is a striking fact that the formulas represented are very evenly spread through a wide range. The distribution

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(4) The possible values must lie at 11 unit intervals. Various relationships exist which may be helpful in determining reasonable values of y, *e. g.*, for any compound containing carbon, hydrogen, oxygen and reduced nitrogen $y = 2x + 2 - 2\alpha + b$, where α is the number of rings and/or double bonds and the other terms have the meanings previously assigned.

is approximately even from the values 6 to 16 inclusive and about 27% of the formulas lie outside this range. In all cases observed throughout the whole table where the oxidation equivalent values lie close together the formulas represented differ materially in molecular weight, nitrogen content or in some cases in degree of unsaturation as previously explained.

Use in Determining Hydrogen Content.—Whether a sample constitutes a pure compound or not, if it contains only carbon, hydrogen and oxygen (plus other elements that may be determined and corrected for), its hydrogen content can be determined accurately by analysis for carbon and for its oxidation equivalent. Strebinger,[1] from the oxidation requirements of the elements, calculated (using slightly different notation and uncorrected values) that $8/3 \cdot \%\ \mathrm{C} + 7.93 \cdot \%\ \mathrm{H} - \%\mathrm{O} = \%\mathrm{O_R}$ where $\%\mathrm{O_R}$ is the oxygen requirement in grams per hundred grams of sample. Combining this with the relationship that for a compound or residue under consideration the sum of the carbon, hydrogen and oxygen percentages is equal to 100, we obtain

$$\%\mathrm{H} = (\%\mathrm{O_R} + 100 - 11/3 \cdot \%\mathrm{C})/8.93$$

The molecular formulas of certain compounds (particularly sterols) have been in doubt because the hydrogen percentage could not be determined with sufficient certainty so as to make possible a definite choice between two values which lie 4–5 parts per hundred apart. Fisher[5] indicates the "allowed" error for a hydrogen analysis in macro combustions to be 2 parts and never over 3 parts per hundred.

Carbon can be determined much more accurately than this[5] without undue complication in apparatus. It should be possible by careful work to determine both the carbon percentage and the oxidation equivalent value with an error of one part per thousand. This would allow a calculation of the hydrogen content (*e. g.*, of cholesterol) with an error of not more than 5 parts per thousand even if the errors in analysis were in opposite directions thus producing the maximum error in the value for hydrogen percentage.

Other Applications.—Very small samples of tissue, bacteria, etc., can be subjected to a proximate analysis for "protein," carbohydrate and fat by combining an oxidation equivalent analysis with a determination of nitrogen on a micro scale. For carbohydrate (starch or glycogen) the oxidation equivalent value is 13.5; for a protein (egg albumin) it is 10.47; for a fat (triolein) it is 5.53. The proportions in a mixture can be calculated readily from the data mentioned above. The method of oxidation equivalents also has a possible application in the determination and characterization of organic matter in soils and in water.

The writer wishes to express his thanks to Professor W. E. Milne, who has been kind enough to consult with him freely regarding the mathematical aspects of the problem, and to Professor Bert E. Christensen, who was early convinced of the value of the method and agreed to collaborate on experimental methods.

Summary

Equations are given by which the molecular formula of a compound can be calculated from its molecular weight and the amount of oxygen required for its complete combustion. The use of oxidation equivalent data as a substitute for that obtained from carbon and hydrogen combustions is discussed.

CORVALLIS, ORE. RECEIVED AUGUST 20, 1936

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(5) Fisher, "Laboratory Manual of Organic Chemistry," John Wiley and Sons, Inc., New York, 1931, p. 286.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

Organic Oxidation Equivalent Analysis. II. By the Use of Iodate. (Micro and "Sub-micro" Methods)

BY ROGER J. WILLIAMS, EWALD ROHRMAN AND BERT E. CHRISTENSEN

The use of potassium iodate in slightly diluted sulfuric acid recommended itself to Strebinger[1] as a suitable process for determining the amount of oxygen used up in the oxidation of a compound because its use avoids the production of carbon monoxide, and allows for a simple back titration of the unused oxidizing agent. Stanek and Nemes[2] without cognizance of Strebinger's work used potassium iodate in concentrated sulfuric acid under similar conditions in a complicated system of micro organic analysis in which "oxygen consumed," carbon, nitrogen and halogens were determined.

We have investigated the quantitative oxidation of organic compounds by potassium iodate in concentrated sulfuric acid and have found the method to be applicable under suitable conditions to most carbon–hydrogen–oxygen compounds and to certain nitrogen compounds, but that it has definite restrictions other than those indicated by the work of the authors mentioned above. We shall, for economy of space, leave out data which fall in line with the observations of Strebinger and Stanek and Nemes and give in more detail the results which supplement or are contradictory to theirs.

Danger of Oxidizing Nitrogen.—While under the conditions used by Stanek and Nemes there is probably not a serious danger of oxidizing nitrogen, Strebinger's conditions are more unfavorable in this regard. On the basis of numerous duplicate analyses we find that when nitrogenous compounds are analyzed and the sample is increased up to the concentration used by Strebinger there is an extra "oxygen consumption" which must be due to the oxidation of ammonia.

That the danger lies in the accumulation of liberated iodine was shown by several experiments. For example three samples of acetanilide 4.02 mg. (pipetted in solution in test-tubes and evaporated in vacuum) were treated alike except that to the second and third were added 10 and 100 mg., respectively, of iodine. Oxidation was for thirty minutes at 185°. The oxygen consumptions in the three cases were, respectively, 0.15% low, 0.45% high and 8.0% high, indicating that iodine brings about additional oxygen consumption. In order to avoid this possibility we have used 3–4 mg. samples and 5 ml. of concentrated sulfuric acid, which reduces the concentration to about one-half that used by Stanek and Nemes and to about one-fifth that used by Strebinger.

Failure to Oxidize Nicotinic Acid.—Stanek and Nemes[2] pointed out that quantitative oxidation of nitrogen compounds with iodate is accomplished only when the nitrogen can be determined by the Kjeldahl method. Nitro compounds, hydrazones and heterocyclic nitrogen compounds fail to yield satisfactory results. When we applied the method to nicotinic acid (185° for twenty minutes) 3.8 and 4.1% oxidation resulted in duplicate analyses. Raising the temperature sufficiently to oxidize the ring without oxidizing nitrogen and introducing other complications does not seem feasible.

Acetates.—As a result of a rather extensive study we conclude that *generally speaking* acetic acid is the most difficultly oxidized organic compound with which we have been concerned. However, acetic acid is oxidized with iodate more easily than nicotinic acid, though when permanganate is the oxidizing agent the situation is distinctly reversed. Succinic acid is likewise difficult to oxidize (with iodate or dichromate) but not as difficult as acetic acid.

Many organic substances liberate iodine in the cold when the sulfuric acid–iodate reagent is used. Succinic acid required four minutes in a bath at 185° before appreciable iodine color appeared. Acetic acid required eight minutes at this temperature to bring about visible iodine liberation. The difficulty of oxidizing acetic acid is further shown by the fact that acetanilide cannot be oxidized completely with iodate at 185° in twenty minutes (Tables I and II). The aniline portion of the molecule is easily oxidized, however, and liberates iodine from iodate in the cold.

Phthalate Oxidations.—A further limitation of the method appeared when we attempted to apply it to potassium acid phthalate and phthalic anhydride. Strebinger reported one satisfactory analysis of phthalic acid and one of a naphthol. Stanek and Nemes reported no analyses of phthalates. Two determinations on potassium acid phthalate yielded results indicating an 80% and a 75% oxidation, respectively. In the second one of these analyses the sample was dissolved carefully before heating or introduction of iodate took place, but the result was even farther in error than the first. Oxidation of phthalic anhydride at the same temperature (185°) for thirty minutes instead of twenty minutes as used above, resulted in only 74% oxidation. Potassium acid phthalate appears, however, to be oxidized completely at higher temperatures. Thirty minutes at 200° brought the oxygen consumption to about 88% of the theoretical, while at 210° the oxidation appeared 99.3% complete in the same time. At 220° for thirty minutes nearly 2% too much iodate was used. This excess may have been due to thermal decomposition of iodic acid[2] or to oxygen consumption by the sulfuric acid used.

Use on a Micro Scale.—The data given in Table I were obtained as a result of a series of analyses none of which was

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(1) Strebinger, *Z. anal. Chem.*, **58**, 97–114 (1919).

(2) Stanek and Nemes, *ibid.*, **95**, 244 (1933).

TABLE I

MICRO ANALYSES

Substance	Wt. of sample, mg.	Time heated, min.	Wt. iodate used, mg. (plus 5 cc. H_2SO_4 and .2 cc. H_2O)	Iodate used up, mg.	Iodate used above blank	Theoretical	Error, %
Blank	...	40	59.005	0.556	....	....	.....
Blank	...	40	52.072	.582	....	....	.....
Blank	...	40	43.652	.514	....	....	.....
Sucrose	3.798	20	71.477	23.317	22.766	22.788	−0.096
Sucrose	3.536	20	86.026	21.801	21.250	21.216	+0.16
Acetanilide	3.095	20	96.028	34.582	34.031	35.314	−3.62
Acetanilide	2.953	20	92.350	32.690	32.141	33.694	−4.6
Sucrose	4.213	40	101.69	26.122	25.571	25.278	+1.16
Sucrose	3.905	40	91.283	24.263	23.712	23.430	+1.2
Acetanilide	2.982	40	96.892	34.259	33.708	34.025	−0.93
Acetanilide	3.297	40	100.73	38.228	37.677	37.619	+0.15

TABLE II

"SUB-MICRO" ANALYSES

Substance	Wt. of sample, mg.	Time heated, 185° min.	Wt. iodate used plus 1 cc. concd. sulfuric acid	Iodate used up, mg.	Iodate used above blank	Theoretical	Error, %
Blank	..	20	15.054	0.029	...	...	....
Blank	..	20	16.294	.018	...	...	....
Blank	..	40	15.248	.030	...	...	....
Acetanilide	0.438	20	17.849	4.790	4.764	4.99	−4.5
Acetanilide	.565	20	18.288	6.258	6.232	6.447	−3.3
Acetanilide	.536	20	18.726	5.851	5.825	6.116	−4.8
Valine	.459	20	16.521	4.000	3.974	4.030	−1.4
Valine	.608	20	16.003	5.258	5.232	5.338	−2.0
Acetanilide	.567	40	17.415	6.504	6.478	6.469	+0.14
Acetanilide	.539	40	18.236	6.150	6.124	6.150	−0.42
Acetanilide	.446	40	18.597	5.052	5.026	5.089	−1.2
Valine	.403	40	17.443	3.584	3.558	3.538	+0.56
Valine	.570	40	17.007	4.988	4.962	5.004	−0.84

discarded. It is given in some detail to show how closely duplicates may be expected to check and also to show that the method of analysis must be modified slightly for different types of compounds. A twenty-minute heating period gives remarkably accurate results with sucrose but with acetanilide (which is admittedly an extreme case due to acetic acid formation) large errors result using this length of time. A forty-minute period gives acceptable results with acetanilide but with sucrose this extra period throws the results off somewhat. Probably for general use thirty minutes gives the best results but it seems clear that modifications, dependent upon the character of the material analyzed, must be made to obtain the most accurate results. It seems likely from our experience that at least in the case of easily oxidized compounds (carbohydrates, for example) the iodate method may yield precise results. As a rapid micro method for obtaining results of moderate accuracy it should be useful and with materials of biological origin (with the exception of certain alkaloids) it should be applicable and useful.

Use on a "Sub-micro" Scale.—One of the reasons for being interested in the application of this method was the possibility that it might be used for analyzing samples weighing not more than a fraction of a milligram—or the order of one-tenth that used for ordinary micro combustions. That this is possible with certain types of compounds is indicated by the data presented in Table II. These constitute a consecutive series of determinations with no analysis excluded. The samples to be analyzed were each weighed into test-tubes in the form of a water solution, the weighed amount of iodate was added and the solution was evaporated overnight in a vacuum desiccator. For weighing the solutions (on an ordinary balance) bottles of the solution containing a ground glass medicine dropper were weighed before and after the samples were removed. The titrations were carried out with an ordinary buret using 0.025 *N* thiosulfate. The iodate can be weighed conveniently in solution with saving of time and as a result ten analyses can be completed within about one working day, with an overnight period allowed for evaporation.

Procedure.—The procedure which we recommend for "micro" work is exceedingly simple. The sample which weighs 3 or 4 mg. is introduced into a test-tube along with 5 ml. of sulfuric acid, 0.2 ml. of water, and sufficient potassium iodate to constitute at least 100% excess. Both the sample and iodate can be weighed in the form of water solution if desired and then evaporated. It is necessary that the sample and the iodate be well distributed throughout the medium before heating is begun. Whether or not the acid is diluted with a small percentage of water seems to make no material difference in the results. The samples are heated in a sulfuric acid bath to 185° for twenty to forty minutes (see above) after which the mixture is transferred to an Erlenmeyer flask, diluted with 60 ml. of water and steamed for five minutes using a suitable source of clean steam. The inlet tube for the steam is then rinsed with 40 ml. of water and after cooling 0.75 g. of sodium bicarbonate is added to the flask to reduce acidity and give an atmosphere of carbon dioxide; 1.5 g. of powdered potassium iodide is added and the iodine which is freed is titrated with 0.1 *N* sodium thiosulfate. Most of the precautions which have to be observed are those involved in iodometric titrations in general and are not properly presented or discussed here. The purest available chemicals including "Kahlbaum" potassium iodate and sulfuric acid were used. When the samples were very small and 0.025 *N* thiosulfate was used, suitable corrections were applied for the "titration error."

Summary

Oxidation with iodate in concentrated sulfuric acid and back titration of the unused iodate constitutes a method (which, however, is not perfectly general) for determining the amount of oxygen necessary for the complete oxidation of organic compounds (see first article in this series). There is danger of oxidizing nitrogen, however, if the concentration of the sample is too high. Phthalates are oxidized with difficulty and nicotinic acid, for example, is oxidized very little. It can, however, be applied rather widely to compounds of various types and accurate analyses are possible with samples weighing a fraction of a milligram.

CORVALLIS, OREGON RECEIVED AUGUST 20, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

Organic Oxidation Equivalent Analysis. III. General Method Using Dichromate

BY BERT E. CHRISTENSEN, ROGER J. WILLIAMS AND ANNE E. KING

Dry combustion methods have been devised for determining the amount of oxygen consumed in the oxidation of organic compounds,[1-3] but either they are inaccurate or else involve a complicated apparatus and exacting technique in operation. Wet combustion, if applicable, should involve simpler apparatus and easy experimental methods.

Of the available agents for wet combustion which are obtainable in pure form, potassium iodate and potassium dichromate are outstanding. The use of iodate has been studied[4] and found to be of somewhat restricted value. Potassium dichromate has been used for the determination of oxygen consumed during combustion but if employed at relatively low temperatures[5] (100° or thereabout) is applicable to the oxidation of only a few types of compounds. If used at a sufficiently high temperature to bring about the complete oxidation of compounds generally, free oxygen is invariably produced in considerable quantity accompanied by the formation of carbon monoxide[6] in many cases (oftentimes even at low temperatures). This eliminates the possibility of determining the unused oxidizing agent directly by back titration.

This study was directed toward the perfection of a method using dichromate under conditions which would oxidize organic compounds generally, yet allow for an evaluation of the whole of the unused oxidizing agent (including oxygen gas) and eliminate or correct for the carbon monoxide produced.

It is obvious that many different media and conditions could be employed for the oxidation with dichromate. We have investigated the use of phosphoric acid, sulfuric acid and mixtures of the two. Phosphoric acid (85%) has certain advantages, particularly in that it prevents the formation of insoluble chromous oxide, but its use in connection with nitrogenous compounds is not feasible due to oxidation of ammonia. In this Laboratory it was found that ammonia is almost quantitatively converted to the nitrate in a phosphoric acid medium (a fact which as far as we know has not been previously recorded). Slightly diluted sulfuric acid seems to be most favorable[7]

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(1) Glockler and Roberts, THIS JOURNAL, **50**, 828 (1928).

(2) W. R. Kirner, *Ind. Eng. Chem., Anal. Ed.*, **6**, 358 (1934).

(3) W. R. Kirner, *ibid.*, **7**, 363 (1935).

(4) Williams, Rohrman and Christensen, THIS JOURNAL, **58**, 291 (1936).

(5) Simon and Guillaumin, *Compt. rend.*, **175**, 525 (1922).

(6) I. K. Phelps, *Am. J. Sci.*, **4**, 372 (1897).

(7) H. C. S. Snethlage, *Rec. trav. chim.*, **54**, 651 (1935).

and was used in the work here reported. If five volumes of sulfuric acid are diluted with one volume of water, chromous oxide is not precipitated enough to cause serious inconvenience.

Preliminary experiments indicated that for practically all compounds satisfactory oxidation takes place if the temperature is brought to the point where oxidation is vigorous for a few minutes and then raised and held at 165° for twenty minutes. In the case of a few compounds, when the vigorous oxidation (which is easily noted) fails to take place below 165°, it is necessary to modify the heating so that the ultimate temperature is perhaps 10° above the point where the reaction appears to be vigorous. Temperatures up to 200° were not sufficient to cause appreciable oxidation of ammonia.

Considering the danger of escape of volatile, difficultly oxidized compounds (particularly acetic acid) on the one hand and the size of the correction due to dissolved gases on the other, it was deemed advisable to use 12 ml. of medium per 1.5-g. charge of dichromate.

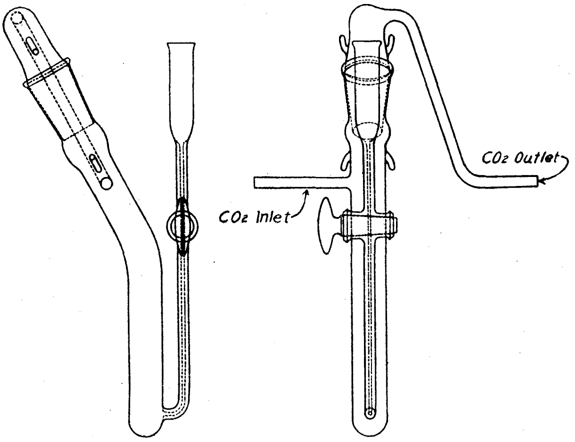

Fig. 1.

Two methods were available for the determination of the unreduced dichromate. The simplest procedure involves the thermal decomposition of the excess dichromate and the measurement of all the unused oxidizing agent as oxygen gas. However, in order to carry out the process in a reasonable length of time such high temperatures are required that ammonia if present, is oxidized. This makes the method inapplicable to nitrogenous compounds, and we were forced to determine the unreduced oxidizing agent by back titration. This was done iodometrically.

A cause of difficulty at this point is the fact that during the oxidation and partial decomposition of the dichromate small amounts of an intermediate product (perhaps perchromic acid or $Cr_2(SO_4)_5$[8]) are invariably formed which causes low results on titration. This was obviated by diluting the medium after oxidation with 12 ml. of 6 N sulfuric acid and boiling gently for five minutes. By this means complete recovery was consistently obtained when the oxygen gas collected and the unchanged dichromate were both taken into account.

We have found it impossible to prevent the formation of carbon monoxide while certain compounds (notably carbohydrates) are being oxidized. To avoid error due to this cause, the carbon monoxide may be oxidized to carbon dioxide with the oxygen which is evolved. This has been accomplished in this work by introducing a chamber containing a platinum spiral heated to dull red heat, into the train between the bubble counter and the oxygen buret, or by running the whole sample of gas after collection in the buret into a slow combustion pipet until all carbon monoxide has been oxidized.

Apparatus.—As some carbon monoxide is liable to be formed and large amounts of oxygen are always evolved during oxidation, it is necessary to utilize a closed system whereby these products can be retained. The apparatus used is simple and consists of (1) a Kipp generator for carbon dioxide production, (2) a reaction vessel of special design, (3) a bubble counter, (4) a gas buret (nitrometer), and (5) a slow combustion pipet.

The reaction vessel[9] is pictured in Fig. 1 and is made using a Pyrex No. 20 standard taper joint. The Kipp generator is charged with marble and air-free concentrated hydrochloric acid containing about 20% dissolved calcium chloride, in order that the carbon dioxide shall be as pure as possible; the bubble counter is one of the usual type but constructed so that there is no inverted pocket where gas may be retained; the gas buret is an ordinary Schiff nitrometer and the slow combustion pipet is of the type described by Engelder.[10]

The reaction vessel is heated by means of a special bath, which has been found very convenient, composed of 1 part of metaphosphoric acid and 4 parts of sirupy phosphoric acid.[11]

Procedure.—The reaction vessel is charged with a weighed quantity (about 1.5 g.) of potassium dichromate of known purity. The stopcock on the vessel is lubricated with phosphoric acid. Twelve ml. of a 5–1 (by volume) mixture of sulfuric acid and water is then introduced into

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[8] Ball and Crane, THIS JOURNAL, **55**, 4860 (1933).

[9] This unit can be purchased from the Corning Glass Works, Corning, New York.

[10] Engelder, "Gas, Oil and Fuel Analysis," John Wiley & Sons, Inc., New York, 1931, p. 30.

[11] Christensen and King, *Ind. Eng. Chem., Anal. Ed.*, **9**, 194 (1936).

the reaction vessel through the capillary. The vessel is connected to the Kipp generator in such a position as to permit a porcelain boat to rest near the mouth of the vessel.

The porcelain boat containing a weighed sample to be analyzed (about 100 mg.[12]) is placed at the upper end of the reaction vessel. The seal is lubricated with sirupy phosphoric acid, closed and held together with small steel springs. The bubble counter is connected on the one hand to the outlet tube of the vessel and on the other to the gas buret. For connections sound heavy-walled rubber tubing (2 mm. internal diameter), well lubricated with water, is used.

In order to simplify the assembling of the apparatus the gas buret should be suspended from the top so that the position of the lower end can be adjusted easily.

The system is flushed with a moderate stream of carbon dioxide for about ten minutes; in the meantime the gas buret is charged with 30% potassium hydroxide solution which has been saturated previously with oxygen at room temperature. The flushing is complete when, as in the ordinary Dumas method for nitrogen, the bubbles are negligibly small (about 0.2 mm. in diameter).

The reaction vessel is now rotated to a position about 15° from vertical; this allows the boat and contents to slide into the reaction mixture, and the heating may be started. The bath is adjusted to surround the lower 5-cm. portion of the vessel and its temperature raised slowly (principally to avoid breaking the bath container since the bath mixture is viscous at first) until the oxidation proceeds vigorously. As indicated above, the bath mixture is in most cases held at approximately even temperature for two to five minutes and is then heated to about 165° for twenty minutes. The whole heating process as contrasted with that of carbon and hydrogen combustions is completed with a minimum of care since the bath temperature is regulated easily and, as a result of continuous evolution of gas, the reacting solution boils vigorously without any tendency to superheat or bump.

After the heating time has elapsed the bath is removed and 12 ml. of 6 *N* sulfuric acid is added through the capillary. The reaction mixture is boiled gently for five minutes using a free flame. The residual oxygen is flushed from the system for about four minutes or until the bubbles are negligibly small.

The gas buret is detached and connected to the slow combustion pipet where the carbon monoxide which may have been formed is oxidized by oxygen evolved during the oxidation. The gas is then transferred back to the nitrometer and allowed to stand in a room of even temperature until the volume remains constant.

In the meantime the contents of the reaction vessel are washed into a 500-ml. volumetric flask with boiled water. A 100-ml. aliquot is removed; to it are added 2 g. of sodium bicarbonate and 4 g. of potassium iodide. This is allowed to stand for a half hour in a stoppered bottle, diluted to about 300 ml. with boiled water, and titrated with 0.1 *N* sodium thiosulfate.[13]

The analysis is thus completed in less than two hours. A considerable part of this time (during the heating and waiting for the final titration) can be utilized for the preparation of samples for the next analysis, or completion of other analyses if more than one apparatus is available. It only remains to calculate the amount of oxygen (in milliequivalents) in the buret and the milliequivalents of residual oxidizing agent and subtract these from the milliequivalents of dichromate originally used. This gives the milliequivalents used by the sample. In calculating the milliequivalents of oxygen gas it is of course necessary to make the usual corrections for temperature, barometric pressure, vapor pressure of the potassium hydroxide solution[14] and calibration of the buret. In addition there is a small correction for the air which originates in the sulfuric acid solution or from the Kipp generator. This amounts to 0.3 to 0.4 ml. and as it is practically constant needs to be determined only occasionally. This is done by passing the gas into a Hempel pipet charged with alkaline sodium hydrosulfite, and measuring the unabsorbed gas. The air correction is calculated as five-fourths of the residual nitrogen.

Discussion and Results.—The results given in Table I are representative of those obtained under ordinary laboratory conditions. Partly through

TABLE I

RESULTS OF ANALYSES

The first nine analyses recorded were run with the platinum spiral combustion chamber in the combustion train behind the gas buret. This took the place of the slow combustion pipet.

Substance analyzed[a]	Percentage errors in milliequivalents of oxygen used. (Successive analyses)				
Succinic acid	+0.06[b]	+0.09	+0.30	+0.97	−0.11
Sucrose	.00	− .56[c]			
Potassium acid phthalate	− .17	− .31			
Sucrose	+ .10	+ .02			
Potassium acid phthalate	+ .47	+ .14			
Acetanilide	+ .45	− .51	−0.11	+0.22	
Benzoic acid	+ .22	+ .54	−2.06[d]		
	+ .03	−2.05[d]	+0.21	+0.19	
Leucine	+ .15	+0.06			
Quinoline	− .58[e]	− .92[e]			
Benzidine	+ .17	+ .68	+0.96		

[a] The samples used varied from about 0.15 g. for succinic acid down to 0.05 g. for benzidine. [b] The temperature of this combustion was 200° instead of 165°. [c] In this analysis, carbon monoxide was found to have escaped oxidation. The amount was determined and the value corrected accordingly. [d] The difficulty in these two benzoic acid determinations was found to be due to too rapid flushing and a consequent entrainment of some finely powdered benzoic acid which escaped oxidation. This defect was carefully guarded against in the last two analyses. [e] This compound was difficult to oxidize and the temperature was raised to 185° and held there for over thirty minutes. The indications are that even this may not have been entirely sufficient.

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(12) If the material is of a waxy or oily consistency or is known to be a compound of high oxygen requirement, the sample should be reduced somewhat (even to about half this size); whereas, if it is known to be a highly oxygenated compound such as a carbohydrate, the size of the sample may be increased by 50% or more.

(13) Willard and Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, 1933, p. 187.

(14) "International Critical Tables," McGraw-Hill Book Co., Inc., New York.

intention and partly through necessity most of the analyses were run under conditions far from ideal. After the proper conditions had been established, the method, in the hands of a relatively inexperienced student using ordinary balances, weights, volumetric apparatus, and chemicals, gave results which are far from unsatisfactory.

All analyses made after the method was established in its present form are included in Table I except exploratory tests on materials known to be impure, such as paraffin, and tests on certain compounds (particularly asparagine) which were found later to be impure and variable in composition. It seems to be a significant fact that we have experienced no difficulty in obtaining *highly satisfactory results with every compound the standard of purity of which was unusually high* (succinic acid, potassium acid phthalate, sucrose, acetanilide, benzoic acid).

Duplicate analyses of nicotinic acid (which is almost untouched by the iodate method[7]) gave consistent results which were only slightly low. This sample upon further investigation was found to be impure. Subsequent work with quinoline indicates that the method apparently is applicable to compounds containing the pyridine nucleus.

Analyses of paraffin showed it to be difficult to oxidize, apparently not because of its stability toward the oxidizing agent but because of its insolubility. Using the ordinary procedure it is over 90% oxidized, but after the reaction mixture cools small flakes of unchanged paraffin are visible on the surface. The indications are that by modifying the procedure accurate analyses could be obtained even on paraffin.

On the basis of the above facts we are of the opinion that by using extra precautions and precision equipment it should be possible to obtain highly precise results in the analysis of organic compounds generally. Under ordinary conditions one can obtain results which are in error less than 5 parts per thousand, which is satisfactory for the purposes outlined in the first paper of this series.

Preliminary experiments indicate that compounds containing sulfur may require some special treatment to obtain accurate results, though values which are at least approximately correct are obtained using the method as here outlined. The adaptation of the method as outlined to a micro scale has led to irregularities presumably associated with the formation of intermediate reduction products of dichromate, which as yet we have been unable to eliminate.

Summary

A method for the accurate determination of the oxidizing agent required for the complete combustion of organic compounds, using potassium dichromate as the oxidizing agent, is described.

In accordance with equations developed in the first paper in this series, this determination can be substituted in the majority of cases for a combustion analysis.

Its advantages over combustion analyses are: (1) considering all preliminary preparations, it is quicker; (2) it uses a minimum of special equipment and none which cannot readily be made in the laboratory; (3) it requires no special catalysts or materials which are likely to introduce complications; (4) it involves the simplest technique and no careful control of heating or gas evolution; (5) it, when taken in conjunction with an accurate carbon determination, makes possible a more accurate determination of hydrogen than has hitherto been possible under ordinary analytical conditions.

Corvallis, Ore.

Received August 20, 1936

[CONTRIBUTION FROM THE NICHOLS CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

Quaternary Derivation of Pyridyl Ethers. Onium Compounds. XVI

BY R. R. RENSHAW AND R. C. CONN[1]

In previous publications the synthesis[2] and the pharmacological effects, determined by Reid Hunt,[3] of certain onium derivatives of pyridine, piperidine and pyrrolidine have been described. From these data and other work it was found that many of these quaternary derivatives without substitution on the cyclic carbon atoms acted on the autonomic nervous system producing the acetylcholine effect or the nicotine actions or both. Thus the carbethoxypyridinium ion was 75 times as active as choline in producing the acetylcholine effect and the beta - phenoxyethyl - methylpyrrolidinium ion half as active as nicotine in causing a rise of blood pressure.[3b]

A limited number of quaternary compounds having substituents on the cyclic carbon have been synthesized and studied. With the exception of quaternary derivatives of nicotine acid ester[3a,4] and its hydrogenated product[3a,4a] most of these showed little or no effect on the autonomic system even though the groups present[3b] (amide and acetamino) would produce these effects when introduced in the choline structure. Since the number of compounds of this latter type which have been investigated was so small we began in this Laboratory the preparation of a series of ethers, of choline type esters and of carbaminoyl derivatives of these heterocycles. The latter two fields will be the subject of papers to follow.

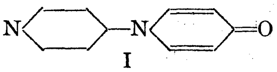
2-Pyridyl Ethers.—A number of 2-pyridyl ethers were prepared by heating 2-bromopyridine with the alkali salts of alcohols and phenols. Yields of 90% and better of 2-aryloxypyridines were obtained with no indication of any N-arylpyridines being formed. This is a more satisfactory method than that reported by Chichibabin[5] for the preparation of 2-phenoxypyridine, the only alpha-substituted pyridine reported in the literature. He obtained a mixture of ortho- and para-pyridyl phenols together with some 2-phenoxypyridine by warming 2-pyridyl diazotate with phenol.

The reaction was extended to include the use of alkylated phenols, resorcinol as a typical dihydric phenol and benzyl alcohol. With resorcinol, although the quantities of reactants were such as to give the mono-ether, only the dipyridoxy ether and an unidentified, very difficultly soluble, red crystalline product were obtained.

These 2-pyridyl ethers are very weak bases. This is probably due to the proximity of the aryloxy grouping to the ring nitrogen. They fail to deposit picrates from either ether or benzene solution and may be steam distilled from solutions of mineral acids. This behavior is in contrast to that of the corresponding 3- and 4-substituted ethers of pyridine which form stable picrates and salts of mineral acids. Alkyl halides add much more slowly to the 2-substituted ethers than to the corresponding 3- and 4-substituted derivatives although the final yields of pyridinium halides are essentially the same. 2-Pyridyl-benzyl ether did not yield a methiodide.

4-Pyridyl Ethers.—4-Pyridyl ethers were prepared by the interesting method of Koenigs and Greiner[6] whereby 4-pyridylpyridinium dichloride is heated with an alcohol or phenol in the optional presence of an acid binding agent. A number of previously reported ethers were prepared in this way and, in addition, one new alkoxy ether, 4-*n*-butoxypyridine, was prepared.

Methyl and ethyl iodide were also added to N-4′-pyridyl-4-pyridone (I) first prepared by Arndt


I

and Kalischek[7] by warming 4-hydroxypyridine with acetic anhydride. Although first considered by them to be 4,4′-dipyridyl ether, Arndt[8] later showed it to have the N-pyridyl-pyridone structure (I). We have found that, whereas I forms dibasic salts with hydrochloric, chloroplatinic and chloroauric acids, it will only add one mole of alkyl halide. This may be due to a steric effect or to the decreased basicity of the pyridone nitrogen.[9] Further confirmation for the pyridone structure

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(1) This is the first paper constructed from a portion of a thesis presented by R. C. Conn, June, 1935, for the degree of Doctor of Philosophy at New York University.

(2) Renshaw and Shand, THIS JOURNAL, **54**, 1474 (1932).

(3) Hunt and Renshaw, (a) *J. Pharmacol.*, **35**, 75 (1929); (b) **37**, 177 (1929).

(4) (a) Loewy and Wolffenstein, *Therap. Gegenwart*, **61**, 287 (1920); (b) Haramaki, *Biochem. Z.*, **130**, 267 (1922).

(5) A. E. Chichibabin, *J. Russ. Phys.-Chem. Soc.*, **50**, 502 (1918).

(6) Koenigs and Greiner, *Ber.*, **64**, 1049 (1931); German Patent 536,891.

(7) Arndt and Kalischek, *Ber.*, **63**, 592 (1930).

(8) Arndt, *ibid.*, **65**, 92 (1932).

(9) Weitz, Werner and Schwechter, *ibid.*, **59**, 2307 (1926).

lies in the fact that both methiodide and ethiodide are colored.

3-Pyridyl Ethers.—No 3-substituted aryl ethers are reported in the literature and only two (3-methoxy[10,11] and 3-ethoxy[12,13]) alkyl ethers have been prepared.

We have prepared 3-phenoxypyridine in the two following ways:

(1) Pyridine ⟶ 3-pyridyl sulfonic acid ⟶ 3-hydroxypyridine ⟶ 3-phenoxypyridine

(2) 2-Chloro-5-nitropyridine ⟶ 3-aminopyridine ⟶ 3-iodopyridine ⟶ 3-phenoxypyridine

The final step (phenylation) in both these syntheses was carried out according to the method of Ullmann.[14] Method 2 proved to be the more satisfactory because of the better yields and fewer experimental difficulties in the intermediate steps and because of the considerably greater yield in the final phenylation.

Reduction of Ethers.—The catalytic reduction of the methiodides of the three isomeric phenoxypyridines prepared in this investigation was attempted with the hope of obtaining the corresponding phenoxypiperidines for the purpose of physiological study. It was found that both 2- and 4-phenoxymethylpyridinium iodide were reduced with cleavage of the phenoxy grouping, phenol and N-methylpiperidine being formed. This behavior is consistent with results obtained by other investigators. Graves[15] found that 2-methoxypyridine underwent a similar reductive cleavage with the formation of methyl alcohol and piperidine. Koenigs and Neumann[16] reduced 4-pyridyl ethers with sodium–alcohol and obtained 90% yields of piperidine.

In contrast to the behavior of the 2- and 4-phenoxypyridines, the catalytic reduction of 3-phenoxymethylpyridinium iodide proceeded rapidly and in good yields without loss of the 3-phenoxy group. In one experiment, however, where a comparatively large amount of catalyst was used, a cleavage did take place to an extent of almost 50%. In all cases the reduction product was converted directly into the dimethylpiperidinium compound by warming in alcohol solution with methyl iodide and excess barium hydroxide.

The stability of substituents in the 3-position as contrasted to the lability of 2- and 4-substituted groups is well illustrated by the behavior of these three phenoxy ethers on reduction. Similarly, the reactivity of 2-bromopyridine, which is essentially that of an aliphatic bromide, as contrasted to the inactivity of 3-iodopyridine is to be noted. This behavior is general, the stability and aromatic nature of 3-substituted pyridines being quite marked whereas 2- and 4-pyridyl derivatives are characterized by the lability and often by the anomalous behavior of the substituted groups.

Experimental Part

2-Pyridyl Ethers.—The method of preparation employed for the aryl ethers of this series was as follows: 0.05 mole of 2-bromopyridine,[17] 0.1 mole of phenol and 0.05 mole of anhydrous potassium carbonate were placed in a flask fitted with a long, upright air condenser and heated in a Wood's metal bath at 200–210° for three hours. The contents of the flask were then diluted with water, made strongly alkaline and steam distilled. The distillate was extracted with ether and the extract dried. After removing the ether, the residual oil was vacuum distilled. The yields and boiling points under reduced pressures obtained for these ethers are recorded in Table I.

The reaction with resorcinol was carried out in the same way except that only 0.025 mole of potassium carbonate was used. The reaction initially was quite vigorous, a deep red color developing in the melt. Resorcinol was removed from the reaction mixture by repeatedly washing with hot water until the aqueous extract no longer gave a color test with ferric chloride. The remaining tar was extracted with ether and the ethereal extract dried. A red, solid product remained which could only be dissolved in hot glacial acetic and concentrated sulfuric acids. No identification of this material has as yet been made. On working up the ether extract a solid residue was obtained which was purified by vacuum distillation and recrystallized from a benzene–ligroin mixture from which it separated as pale yellow plates, m. p. 154–156° (corr.). Analysis showed it to be resorcinol di-2-pyridyl ether.

2-Pyridylbenzyl Ether.—A solution of 1.15 g. (0.05 mole) of sodium in 22 g. (0.2 mole) of benzyl alcohol was heated with 7.9 g. (0.05 mole) of 2-bromopyridine for three hours at 210°. Since it was found that ether extraction of a hydrochloric acid solution of the product removed not only benzyl alcohol but 2-pyridylbenzyl ether as well, the two were separated by fractional vacuum distillation.

4-Pyridyl Ethers.—Yields and boiling points of the 4-pyridyl ethers prepared are listed in Table I. The four previously prepared aryl ethers were prepared from 4-pyridylpyridinium dichloride by the method of Koenigs and Greiner.[6] In each case 15 g. of recrystallized 4-pyridylpyridinium dichloride, 40 g. (excess) of phenol and 1.1 equivalents of the sodium salt of the phenol were used. The 70% yield obtained for 4-phenoxypyridine is somewhat better than that (53%) reported by the authors for the same compound. The sodium phenolates used here were

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[10] H. Meyer, *Monatsh.*, **26**, 1311 (1905).

[11] Koenigs, Gredes and Serf, *Ber.*, **61**, 1022 (1928).

[12] O. Fischer and Renouf, *ibid.*, **17**, 1896 (1884).

[13] Weidel and Blau, *Monatsh.*, **6**, 651 (1885).

[14] Ullmann and Sponagel, *Ann.*, **350**, 86 (1906).

[15] T. B. Graves, This Journal, **46**, 1460 (1924).

[16] Koenigs and Neumann, *Ber.*, **48**, 960 (1915).

[17] Craig, This Journal, **56**, 231 (1934).

TABLE I

2- AND 4-PYRIDYL ETHERS

Ether	Yield	B. p. °C.[a]	B. p. Mm.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
2-Phenoxypyridine[b]	92	134–135	11			
2-*o*-Cresoxypyridine	90	156–158	21	$C_{12}H_{11}ON$	7.56	7.71
2-*p*-Cresoxypyridine	92	171.5–172.5	22	$C_{12}H_{11}ON$	7.56	7.76
2-*m*-Cresoxypyridine	83	164–166	20	$C_{12}H_{11}ON$	7.56	7.83
2-Carvacroxypyridine	73	133–134	2	$C_{15}H_{17}ON$	6.16	6.13
Resorcinol di-2-pyridyl ether[c]	38	183–185	3	$C_{16}H_{12}O_2N_2$	10.6	10.5
2-Pyridyl benzyl ether	65	162–164	20	$C_{12}H_{11}ON$	7.56	7.20
4-*n*-Butoxypyridine	37	129–131	25	$C_9H_{13}ON$	9.27	9.7[d]
4-Methoxypyridine[e]	15	95–96[f]	31			
4-Phenoxypyridine	70	157–158[g]	21			
4-*o*-Cresoxypyridine	66	161–162[h]	19			
4-*p*-Cresoxypyridine	67	166–167[i]	22			
4-*m*-Cresoxypyridine	67	124–126[j]	4			

[a] All boiling points are corrected for stem emergence. [b] Chichibabin[5] gives 277–277.5°. [c] Yellow plates, m. p. 154–156° (corr.). [d] Converted directly into the methiodide without redistillation for further purification. [e] Prepared by heating 20 g. of purified 4-pyridylpyridinium dichloride and 20 g. of methyl alcohol in a sealed tube for five hours at 150°. Picrate, m. p. 171–172°. [f] Haitinger and Lieben [*Monatsh.*, **6**, 320 (1885)] give 190.5–191.0° at 738.3 mm. [g] Koenigs and Neumann (*Ber.*, **48**, 959 (1915)] give 134–136° at 10 mm. [h] Koenigs and Greiner[6] give 276–280°. [i] Koenigs and Greiner[6] give 288–290°. [j] Koenigs and Greiner[6] give 284–288°.

TABLE II

ONIUM DERIVATIVES OF PYRIDYL ETHERS

Pyridinium iodide	Crystal form	Yield, %	M. p., °C. (corr.)	Formula	I, %[a] Calcd.	I, %[a] Found	I, %[a] Found
2-Phenoxymethyl-	Four pointed starlike clusters	96	174–175	$C_{12}H_{12}ONI$	40.54	40.55	40.47
2-Phenoxyethyl-	Thin, irregular plates	57	150.5–151.5	$C_{13}H_{14}ONI$	38.81	38.83	38.77
2-*o*-Cresoxymethyl-	Needles	92	186–186.2 (dec.)	$C_{13}H_{14}ONI$	38.81	38.79	38.83
2-*o*-Cresoxyethyl-	Fine, narrow rectangles	69	122–124	$C_{14}H_{16}ONI$	37.21	37.16	37.12
2-*p*-Cresoxymethyl-	Thin, rectangular plates	93	149–150	$C_{13}H_{14}ONI$	38.81	38.75	38.72
2-*m*-Cresoxymethyl-	....	90	145–146.5	$C_{13}H_{14}ONI$	38.81	38.93	38.90
2-*m*-Cresoxyethyl-	....	70	126–126.5	$C_{14}H_{16}ONI$	37.21	37.22	37.19
2-Carvacroxymethyl-	Flat, transparent plates	85	134–135	$C_{16}H_{20}ONI$	34.38	34.20	34.20
3-Phenoxymethyl-	Narrow rectangular plates (yellow)	96	82.5–84	$C_{12}H_{12}ONI$	40.54	40.49	40.56
3-Phenoxyethyl-	Transparent plates	98	136–137	$C_{13}H_{14}ONI$	38.81	38.73	38.79
4-Phenoxymethyl-	Irregular clusters of short, stout plates	68	227.5–228.5	$C_{12}H_{12}ONI$	40.54	40.36	40.52
4-Phenoxyethyl-	Narrow rectangular plates	70	110.5–111	$C_{13}H_{14}ONI$	38.81	38.92	38.93
4-*o*-Cresoxymethyl	Thick needles	100	163–164	$C_{13}H_{14}ONI$	38.81	39.05	39.02
4-*o*-Cresoxyethyl-	Narrow plates	79	148	$C_{14}H_{16}ONI$	37.21	37.10	37.21
4-*p*-Cresoxymethyl-	Irregular masses of short, stout plates	81	163	$C_{13}H_{14}ONI$	38.81	38.88	38.84
4-*p*-Cresoxyethyl-	Long spear-like needles	93	126–126.5	$C_{14}H_{16}ONI$	37.21	37.25	37.24
4-*p*-Cresoxy-β-phenoxyethyl-[b]	Plates	64	129–130	$C_{20}H_{20}O_2NBr$			
4-*m*-Cresoxymethyl-	Irregular clusters of short, thick plates	92	157–158	$C_{13}H_{14}ONI$	38.81	38.69	38.76
4-*m*-Cresoxyethyl-	Irregular clusters of plates	85	128	$C_{14}H_{16}ONI$	37.21	37.21	37.00
4-*m*-Methoxymethyl-	Narrow, rectangular plates	100	145 (dec.)	$C_7H_{10}ONI$	50.60	50.76	50.57
4-*n*-Butoxymethyl-	Plates	100	74–75	$C_{10}H_{16}ONI$	43.32	43.28	43.29

[a] All halogen analyses were carried out by the Fajans method of titration using 0.01 *N* silver nitrate. [b] Obtained as the pyridinium bromide. Calcd. for $C_{20}H_{20}O_2NBr$: Br, 20.70. Found: Br, 20.63, 20.61.

prepared by adding sodium wire to the phenol in benzene, filtering and washing with ether.

4-*n*-Butoxypyridine was prepared by refluxing a suspension of 22 g. of purified 4-pyridylpyridinium dichloride in 400 cc. of *n*-butyl alcohol containing 6.8 g. of sodium. 4-*n*-Butoxypyridine is insoluble in water and possesses an ethereal odor.

Preparation of Onium Derivatives.—The onium derivatives listed in Table II were prepared by allowing a solution of the pyridyl ether in 10 cc. of dry ether and an excess of alkyl iodide to stand at room or slightly elevated temperatures for periods varying from one to six days. Addition of methyl iodide to the 3- and 4-pyridyl ethers proceeded rapidly at room temperature but ethyl iodide added more slowly and the reaction was carried out at 40–50°. Addition to the 2-pyridyl ethers was still less rapid but by heating to 70° satisfactory yields were obtained.

The methiodides of the 4-pyridyl ethers were recrystallized from a hot mixture of Cellosolve and ethyl acetate and the other onium derivatives were recrystallized from hot amyl alcohol–amyl acetate. All were well-defined, crystalline products and were not generally hygroscopic. The low melting point of 3-phenoxymethylpyridinium iodide is interesting and the higher melting point of the corresponding ethiodide (3-phenoxyethylpyridinium iodide) is particularly surprising. Whereas the methiodide tended to form an oil on recrystallization and was appreciably hygroscopic, the ethiodide showed no tendency to form oils, crystallized without seeding and was not appreciably hygroscopic.

4-*p*-Cresoxy-β-phenoxyethylpyridinium bromide was prepared by heating 2 g. (0.001 mole) of 4-cresoxypyridine and 2.2 g. (0.001 mole) of β-phenoxyethyl bromide in dry toluene for three days at 70–80°. The toluene was decanted and the separated oil dissolved in water, the aqueous solution extracted with ether and evaporated to dryness on the water-bath. The residue was dried thoroughly and washed several times with dry benzene. Crystallization was effected by dissolving in absolute alcohol and slowly removing the solvent under reduced pressure. The product was recrystallized from hot Cellosolve–ethyl acetate.

N-4′-Pyridyl-4-pyridone.—This product was prepared by heating 4-hydroxypyridine with acetic anhydride following the directions of Arndt and Kalischek.[7] Considerable difficulty was encountered in obtaining a product melting above 168°, although a sample melting in the range (m. p. 177–178°) given by these authors was obtained. The lower melting product gave a chloroplatinate and chloroaurate which analysis without recrystallization showed to be quite pure. It was therefore used directly for the preparation of onium compounds.

The chloroaurate of the pyridone was obtained as a yellow crystalline powder, m. p. 218–219° (corr.).

Anal. Calcd. for $C_{10}H_9ON_2Cl_4Au{\cdot}2H_2O$: Au, 44.39. Found: Au, 44.36.

The chloroplatinate was obtained as a buff powder melting above 300°.

Anal. Calcd. for $C_{20}H_{18}O_2N_4Cl_6Pt{\cdot}2H_2O$: Pt, 31.59. Found: Pt, 31.55.

This pyridyl-pyridone forms a dihydrochloride which was obtained both by passing dry hydrogen chloride into an alcoholic solution of the base and by evaporating its solution in dilute hydrochloric acid. It was recrystallized from alcohol in which it was only sparingly soluble; m. p. 238° (dec.).

Anal. Calcd. for $C_{10}H_{10}ON_2Cl_2$: Cl, 28.95. Found: Cl, 28.90.

N-(4′-Methylpyridinium Iodide)-4-pyridone.—Methyl iodide was added to N-4′-pyridyl-4-pyridone, both in alcohol and benzene solution. The product obtained by adding ether to the alcoholic solution after twelve hours of heating at 70° was quite impure and it was found that better results could be obtained by carrying out the reaction in dry benzene. A suspension in benzene, in which it is only moderately soluble, was heated with an excess of methyl iodide at 80° for twelve hours. The crystalline methiodide was filtered and the precipitate extracted with hot benzene to remove the non-alkylated product. The yield was 95% based on the quantity of the pyridone used. The methiodide was recrystallized from hot absolute alcohol from which it separated as yellowish-brown, rectangular plates, m. p. 238–238.5° (corr.). Repeated recrystallization and treatment with mercury and Norite failed to change the color. Analysis showed both the product obtained from alcohol and that obtained from benzene to be the monomethiodide.

Anal. Calcd. for $C_{11}H_{11}ON_2I$: I, 40.41. Found: I, 40.25, 40.20.

N - (4′ - Ethylpyridinium Iodide) - 4 - pyridone.—Ethyl iodide was added to N-4′-pyridyl-4-pyridone in benzene solution in the same manner as methyl iodide. The yield of ethiodide was 91% based on the quantity of pyridone used. Recrystallization from hot absolute alcohol gave buff colored rectangular plates, m. p. 134–135° (corr.), which analyzed as the monohydrate. Repeating the preparation and recrystallizing from hot Cellosolve–ethyl acetate gave a product with the same melting point and analysis. Arndt and Kalischek[7] noted the curious tendency of the original pyridyl-pyridone to deposit a crystalline dihydrate from benzene solution when exposed to air.

Anal. Calcd. for $C_{12}H_{13}ON_2I{\cdot}H_2O$: I, 36.68. Found: I, 36.68, 36.73.

3-Phenoxypyridine. Method 1.—Nine and five-tenths grams (0.1 mole) of 3-hydroxypyridine and 5.6 g. (0.1 mole) of potassium hydroxide were heated at 150° to drive off water and a 6-g. excess of 3-hydroxypyridine was then added together with 15.7 g. (0.1 mole) of bromobenzene and 0.2 g. of copper bronze. The mixture was heated at 200° in a flask fitted with a long, upright air condenser. After six hours heating was discontinued and the reaction mixture worked up in the manner given for the 2-pyridyl ethers. The 3-phenoxypyridine obtained was purified by vacuum distillation, b. p. 147–149 at 17 mm. The yield was 4.7 g. or 27%. 3-Phenoxypyridine has the same pleasant ethereal odor possessed by 2- and 4-phenoxypyridine. It, unlike them, is a liquid at room temperature. No appreciable reaction was obtained when anhydrous potassium carbonate was substituted for potassium hydroxide.

Anal. Calcd. for $C_{11}H_9ON$: N, 8.18. Found: N, 8.01.

Method 2.—Ten and two-tenths grams (0.05 mole) of 3-iodopyridine[18] and 6.1 g. (0.05 mole) of potassium phenolate in an excess of phenol were heated with 0.2 g. of copper bronze as before. A yield of 59% of 3-phenoxypyridine was obtained. Using anhydrous potassium carbonate, the yield was 46%.

Reduction of Ethers.—2-(II), 3-(III) and 4-(IV) phenoxymethylpyridinium iodides were reduced catalytically using Adams platinum oxide catalyst and an initial hydrogen pressure of 3 atm. II and III were reduced in alcohol solution but IV, which was quite difficultly soluble in alcohol, was dissolved in water and reduced in this solvent.

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[18] C. Räth, *Ann.*, **486**, 101 (1931).

The reduction products were not isolated directly but converted first into the corresponding dimethylpiperidinium iodides by the addition of methyl iodide and excess barium hydroxide to the alcoholic solution. In the case of IV, the aqueous solution was first evaporated to dryness and the solid residue taken up in alcohol. The alcoholic solution was dried and methyl iodide added as above.

After warming for twelve hours, the solution was filtered and dry hydrogen chloride passed in to precipitate barium chloride. This was filtered and, after shaking the filtrate with anhydrous sodium carbonate, the alcohol was removed and the last bits of solid product precipitated by the addition of ethyl acetate and ether. The products obtained from the reduction of II and IV were recrystallized from ethyl alcohol-ethyl acetate. They melted at 333–335° with decomposition. Analysis and comparison with an authentic sample showed them to be dimethylpiperidinium iodide, m. p. 334° (dec.).[19]

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(19) Wedekind and Oechslen, *Ber.*, **35**, 1076 (1902).

3-Phenoxydimethylpiperidinium Iodide.—The reduction product of III gave a derivative melting, after recrystallization from ethyl alcohol-ethyl acetate, at 177–178° (corr.). It was obtained in the form of small blunt needles which were only moderately soluble in alcohol. Analysis showed it to be the 3-phenoxy derivative. The yield was 87%.

Anal. Calcd. for $C_{13}H_{20}ONI$: I, 38.10. Found: I, 37.97, 38.05.

Summary

1. The preparation of a number of new pyridyl ethers is described.

2. These ethers along with several previously known have been converted into their methyl and ethyl pyridinium salts for pharmacological examination.

NEW YORK, N. Y. RECEIVED OCTOBER 6, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Production of Dihydroxyacetone by the Action of Acetobacter Suboxydans upon Glycerol*

BY L. A. UNDERKOFLER AND ELLIS I. FULMER

Since the discovery by Bertrand[1–3] that his "sorbose" bacterium (*Acetobacter xylinum*) transformed many polyhydric alcohols into the corresponding ketose sugars, several other species of the genus *Acetobacter* have been found to behave similarly. This type of conversion has been studied particularly with reference to the production of *l*-sorbose by the action of the appropriate organism upon sorbitol; the sorbose then serves as the starting point for the synthesis of ascorbic acid. The influence of the concentration of sorbitol upon the production of sorbose by the action of *Acetobacter suboxydans* has been studied quantitatively by Fulmer, Dunning, Guymon and Underkofler.[4] The authors give a brief literature survey and state the reasons for the use of *Acetobacter suboxydans* in the fermentation. The present communication deals with the optimum conditions for the production and isolation of dihydroxyacetone produced by the action of *Acetobacter suboxydans* upon glycerol.

Bertrand[1–3] was the first to report this conversion by *Acetobacter xylinum;* he isolated and identified the material. This reaction by the above organism was also studied by Fischer and Mildbrand[5] and by Bernhauer and Schoen.[6] Other organisms employed for this purpose include *Acetobacter dioxyacetonicum* by Virtanen and Bärlund[7] and *Acetobacter suboxydans* by visser't Hooft,[8] Virtanen and Nordlund,[9] and by Neuberg and Hofmann.[10] The latter authors considerably improved the methods of crystallization of the dihydroxyacetone and recovered 77% of the theoretical yield.

Experimental

Methods.—The culture of *Acetobacter suboxydans* was obtained from the American Type Culture Collection and is listed as No. 621. The stock cultures were carried on malt-extract agar slants. The cultures used for inoculation in these studies were kept active by transfer each forty-eight hours into a medium containing per 100 cc. 0.5 g. of yeast extract (Difco powdered product) and 6 g. of glycerol. Preliminary experiments showed temperatures of 28–30° to be optimum and all subsequent incubations

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* This work was supported in part by a grant from the Industrial Science research funds of the Iowa State College for studies on the fermentative utilization of agricultural products.

(1) G. Bertrand, *Compt. rend.*, **122**, 900 (1896); *Bull. soc. chim.*, [3] **15**, 627 (1896).

(2) G. Bertrand, *Compt. rend.*, **126**, 984 (1898); *Bull. soc. chim.*, [3] **19**, 502 (1898).

(3) G. Bertrand, *Ann. chim. phys.*, [8] **3**, 181 (1904).

(4) E. I. Fulmer, J. W. Dunning, J. F. Guymon and L. A. Underkofler, THIS JOURNAL, **58**, 1012 (1936).

(5) H. O. L. Fischer and H. Mildbrand, *Ber.*, **57**, 707 (1924).

(6) K. Bernhauer and K. Schoen, *Z. physiol. Chem.*, **177**, 107 (1928).

(7) A. I. Virtanen and B. Bärlund, *Biochem. Z.*, **169**, 169 (1926).

(8) F. visser't Hooft "Biochemische onderzoekingen over het Geslacht Acetobacter," Thesis, Delft, 1925.

(9) A. I. Virtanen and M. Nordlund, *Biochem. J.*, **27**, 442 (1933).

(10) C. Neuberg and E. Hofmann, *Biochem. Z.*, **279**, 318 (1935).

were at 28°. It was also found that concentrations of glycerol above 6% gave decreased yields of dihydroxyacetone. There was no appreciable difference between the action on C. P. glycerol and on glycerol which had been distilled in a vacuum. In each case the inoculum consisted of 3 cc. of active (twenty-four to seventy-two hour) culture per 100 cc. of fresh medium; 100 cc. of medium was used in 300-cc. Erlenmeyer flasks.

It has been noted[4] in studies on the production of sorbose by the action of *Acetobacter suboxydans* that disturbing the culture materially reduced the yield. A similar phenomenon was observed with reference to the production of dihydroxyacetone. Hence, each datum presented represents an analysis on a separate flask.

The course of the conversion of the glycerol into dihydroxyacetone was followed by use of the Shaffer–Hartmann[11] method. The dextrose value was multiplied by 1.5 to obtain the value for dihydroxyacetone. This factor was verified on the pure compound and is accurate only if the amount of the dihydroxyacetone in the sample is in the neighborhood of 75 mg. This finding agrees with that of Bernhauer and Schoen.[6]

The Development of the Medium.—In Table I are given the data for the effect of varying concentrations of yeast extract and of potassium dihydrogen phosphate and of various *p*H values upon the yields of dihydroyxacetone. Although analyses were obtained for periods of two to fourteen days, only the results for the seven-day period are given. In all cases incubation beyond the seven-day period did not give increased yields.

TABLE I

THE INFLUENCE OF THE CONCENTRATION OF YEAST EXTRACT AND OF POTASSIUM DIHYDROGEN PHOSPHATE AND OF *p*H VALUE UPON THE PRODUCTION OF DIHYDROXYACETONE BY THE ACTION OF *Acetobacter suboxydans* ON GLYCEROL

I Yeast extract		II KH_2PO_4		III *p*H	
G. per 100 cc.	Yield, %	G. per 100 cc.	Yield, %	*p*H	Yield, %
0.05	57	0.00	87	9.0	0
.10	67	.30	91	8.0	49
.20	72	.60	90	7.0	91
.30	75	.80	89	6.0	91
.40	76	1.00	87	5.5	89
.50	80	1.50	86	5.0	87
1.00	80	2.00	82	4.0	87
				3.0	87
				2.0	0

I. Medium contained per 100 cc.: 6.0 g. glycerol, yeast extract vary. II. Medium contained per 100 cc.: 6.0 g. glycerol, 0.50 g. yeast extract, KH_2PO_4 vary. III. Medium contained per 100 cc.: 6.0 g. glycerol, 0.50 g. yeast extract, 0.30 g. KH_2PO_4, *p*H vary.

The following conclusions may be drawn from the data presented. The medium must contain at least 0.5% of yeast extract. Optimum yields are obtained with concentrations of potassium dihydrogen phosphate of 0.10–0.30%; further addition of the phosphate decreases the yields. The optimum *p*H range is from 5.5 to 7.0.

The Recovery of Crystalline Dihydroxyacetone.—The method of Bertrand[3] did not give significant yields of crystals. The procedure of Fischer and Mildbrand[5] gave beautiful white crystals but the yield was small. The method finally adopted is a modification of that developed by Neuberg and Hofmann.[10] This modified procedure is illustrated by the example given below.

To 1000 cc. of the fermented medium are added 10 g. each of Norite, calcium carbonate and diatomaceous earth, the medium shaken and filtered. The clear filtrate is evaporated below 35°, *in vacuo*, to about 150 cc., 3–4 volumes of absolute alcohol are added, with stirring, and the mixture filtered. Most of the alcohol is evaporated from the filtrate at 30°, *in vacuo*, and the sirup poured into 10 volumes of acetone, stirring vigorously. The turbid solution is allowed to stand overnight, shaken with Norite and filtered. The clear filtrate is evaporated at 30°, *in vacuo*, to a very thick sirup. The remaining water and acetone are removed in a vacuum desiccator over sulfuric acid. The sirup crystallizes spontaneously into an almost solid mass. Seeding the sirup with a few crystals of dihydroxyacetone accelerates the crystallization somewhat but is not required. The crystalline mass is triturated with *cold* absolute alcohol, filtered with suction, and washed with *cold* absolute alcohol until the pure white crystals are obtained. The crystals are dried in a vacuum desiccator. A further yield may be obtained by combining mother liquors and wash liquids from several batches and proceeding as before by evaporating *in vacuo*, pouring into acetone, etc. The first crop is practically pure but it is readily purified further by recrystallization from acetone. By the above procedure over 80% of the dihydroxyacetone, as determined by the Shaffer–Hartmann method, is readily recovered as crystalline dihydroxyacetone.

Summary

A simple procedure has been given for the production of dihydroxyacetone by the action of *Acetobacter suboxydans* upon glycerol and for the preparation of the crystalline product from the fermented medium.

AMES, IOWA RECEIVED NOVEMBER 27, 1936

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(11) P. A. Shaffer and A. F. Hartmann, *J. Biol. Chem.*, **45**, 365 (1920).

[CONTRIBUTION NO. 579 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Remarks on the Spectra of Methyl Cyanide and Methyl Isocyanide[1]

BY RICHARD M. BADGER AND SIMON H. BAUER

The infra-red spectrum of liquid methyl cyanide was investigated several years ago by Coblentz,[2] using rather low dispersion, and more recently Raman studies[3] have been made on this substance and on methyl isocyanide. The data obtained appear never to have been interpreted completely but attention was called by Dadieu[4] to the presence of a frequency shift of around 2200 cm.$^{-1}$ in the Raman spectra of both substances. This he took as evidence for the presence of a triple bond between carbon and nitrogen in both cyanide and isocyanide. Lechner[5] made a simplified coördinate treatment of the molecules in which he assumed that in two of the vibrations the methyl group would behave as a rigid unit, and by the use of two observed frequencies calculated two of the force constants in each. The values of the larger constants so obtained are probably quite reliable and their magnitude is conclusive evidence for a carbon–nitrogen linkage which at least approaches very closely to triple bond in character. The calculation gave less reliable values for the single bond constants of the C–C and C–N linkages, respectively, since there are two vibrations in which both single bond and methyl group participate to a considerable extent, causing Lechner's values to be somewhat too small.

However, at the present time it is not possible to make a much more satisfactory calculation. The authors have attempted a complete normal coördinate treatment of all parallel vibrations, but when using the so-called "valence force" potential function there appear to be no real and probable values of the force constants which yield the observed frequencies. From this it is evident that additional interaction terms must be added to the potential function, but at present there is no very reliable method of estimating their magnitude.

It is the purpose of this paper to discuss in further detail the analysis of the spectra of methyl cyanide and methyl isocyanide, pointing out some facts of special interest, and to present some new data on harmonic bands in the photographic infrared.

In the Raman spectrum of methyl isocyanide all fundamental frequencies appear and no overtones or combinations have been observed. In the cyanide one frequency (1040 cm.$^{-1}$) is absent in the Raman spectrum but may be supplied from the infra-red where it occurs strongly. By comparison with other molecules, particularly the methyl halides, it is possible to make what appears to be a unique assignment of the fundamentals. This is done in Table I in which the vibration types are given an approximate description, and in which a classification is made as to parallel or perpendicular type. This classification of course only has an exact significance in case the molecules in question have an axis of symmetry.

TABLE I

IDENTIFICATION OF THE FUNDAMENTALS IN THE SPECTRA OF METHYL CYANIDE AND METHYL ISOCYANIDE

ν(cm.$^{-1}$)			
Cyanide	Isocyanide	Type	Approximate description
2996	3003	$\perp$	Vibrations principally confined to methyl group
2942	2951	$\parallel$	
1417	1456	$\perp$	
1370	1414	$\parallel$	
2250	2161	$\parallel$	$\mathrm{C{\equiv}N}$ vibration
917	928	$\parallel$	C—C vibration in cyanide, C—N vibration in the isocyanide
1040	1041	$\perp$	Swinging of methyl group with respect to remainder of molecule
376	290	$\perp$	Bending of $\mathrm{C{-}C{\equiv}N}$ group in cyanide and $\mathrm{C{-}N{\equiv}C}$ group in isocyanide

The possession of a threefold axis of symmetry will depend presumably only on whether the $\mathrm{C{-}C{\equiv}N}$ and $\mathrm{C{-}N{\equiv}C}$ groups are linear or not. In the case of the cyanide there seems no reason to doubt that the group is linear since it has been shown that hydrogen cyanide is definitely a linear

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[1] The experimental work described in this paper is a part of a program of research made possible by a grant to one of us (R. M. B.) from the Penrose Fund of the American Philosophical Society, for which it is desired to express appreciation.

[2] William W. Coblentz, "Investigations of Infra-Red Spectra," Carnegie Institution, 1905.

[3] For references see K. W. F. Kohlrausch, "Der Smekal-Raman-Effekt," Julius Springer, Berlin, 1931.

[4] A. Dadieu, *Wien Ber.*, **139**, 629 (1930).

[5] F. Lechner, *ibid.*, **141**, 291 (1932).

molecule,[6] but in the isocyanide there might possibly be some doubt on this point. Lechner's values for the "triple bond" force constants are 1.733 and 1.630 megadynes per cm. for the cyanide and isocyanide, respectively. These may be slightly in error, and their significance is not quite simple since they include certain interaction constants, but they are at least useful in comparing the two molecules which are so similar in many respects. It is evident that the carbon–nitrogen bond is appreciably weaker in the isocyanide than in the cyanide, suggesting that in the former the linkage may not be completely triple bond in character.

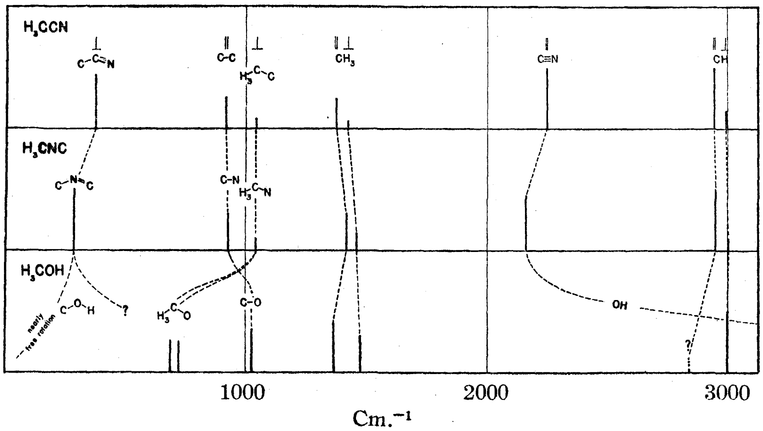

Fig. 1.—Comparison of the Raman spectrum of liquid methyl cyanide and isocyanide (data of Dadieu, etc.) with the infra-red spectrum of methyl alcohol vapor (data of Bartholomé and Sachsse). Missing fundamentals are supplied from the corresponding infrared or Raman spectrum, as the case may be.

It is interesting to compare the vibrations of lowest frequency in the two molecules. The motion in this case is pretty largely a bending of the C—C≡N or C—N≡C groups, and since the mass distribution is so nearly the same in the two cases we can get a rough estimate of the ratio of the force constants involved from the ratio of the squares of the frequencies. We find that the isocyanide bending constant is about 0.6 (or a little less than $^2/_3$) that of the cyanide. At present it is not possible to make any very general statement regarding the bending constants of molecules, but from a recent compilation of data by Penny and Sutherland[7] it appears that they are more or less proportional to the product of the stretching constants of the two bonds involved in the bending. Thus in this deformation oscillation the nitrogen–carbon bond in the isocyanide appears to behave as a double bond. This is probably to be expected since if a double bond structure contributes anything to the ground state of the isocyanide it would be likely to predominate more and more as the molecule is forcibly bent. The question now is whether this trace of double bond character which the bond appears to possess may cause any deviation from linearity in the C—N≡C group in the vibrationless state of the molecule.

Now if we have a bent structure in either the cyanide or isocyanide we should expect a splitting of those frequencies designated as perpendicular in Table I which correspond to degenerate vibrations in a molecule possessing a threefold axis of symmetry. The splitting would undoubtedly be too small to observe in the fundamentals of the internal vibrations of the methyl group, since these are little affected by the remainder of the molecule, but in the two others the separation should be appreciable. The extreme effect would of course be found in the splitting of the low frequency vibration corresponding to the deformation of the cyanide or isocyanide group, since in this case one of the components would take on the character of a torsional motion which would either be of very low frequency or would go over into a more or less free rotation. In order to show what effect may be expected in the absence of a symmetry axis we reproduce in Fig. 1 the infrared spectrum of methyl alcohol vapor, from the data of Bartholomé and Sachsse,[8] together with the Raman spectra of methyl cyanide and isocyanide for the sake of comparison.

By the investigation of both methanol and methanol-*d*, Bartholomé and Sachsse were able to identify a number of fundamental frequencies without uncertainty. They found a separation of 35 cm.$^{-1}$ between the two components of the vibration corresponding to the 1040 frequency in the cyanide and isocyanide, but in the case of the oscillations resulting from the splitting of the vibration analogous to that of lowest frequency in the other substances, neither component could

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

[7] Penny and Sutherland, *Proc. Roy. Soc.* (London), **A156**, 654 (1936).

[8] Bartholomé and Sachsse, *Z. physik. Chem.*, **B30**, 40 (1935).

be identified. From an investigation which the authors have recently made on certain harmonic bands of methyl alcohol[9] it appears probable that one of them has indeed gone over into a nearly free rotation which introduces a new complexity in the rotational structure of the bands.

The great similarity between the spectra of the cyanide and the isocyanide will be noted. From this and the absence of any indication of splitting in the degenerate vibrations it seems reasonable to conclude that the C—N≡C group in methyl isocyanide is linear.

Investigations in the Photographic Infra-red

The authors had hoped that it might be possible to photograph the rotational structure of some of the higher harmonic bands of methyl cyanide and isocyanide and to obtain further information about the structure, but this turned out to be impossible at present. The absorption was very weak except beyond 1 μ and in this region it was not possible to get sufficiently clean plates when using high dispersion, to attempt an analysis. The spectra of the liquid substances and also that of methyl cyanide vapor were, however, photographed under low dispersion (about 70 Å. per mm. at λ 9000) using a path length of 7.6 cm. for the liquids, and 3 meters for the vapor under about one atmosphere pressure. The results are presented in Fig. 2 and Table II. The diagrams were drawn with the use of several microphotometer curves as well as the original plates. The intensities of the bands beyond 1μ may be in considerable error since it is difficult to make estimates in a region in which the sensitivity of the photographic plate is dropping off rapidly with increasing wave length. For the same reason the maxima in this region may be slightly in error.

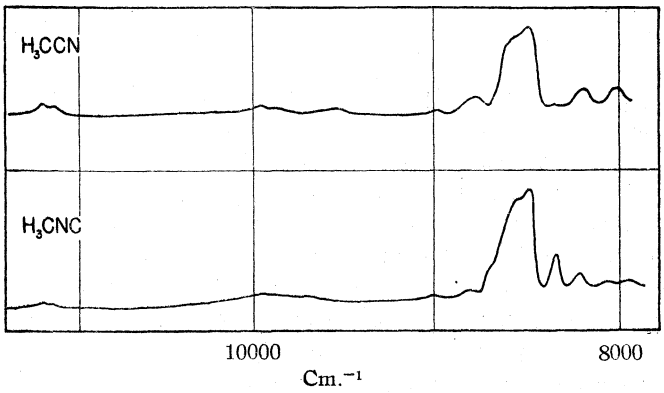

Fig. 2.—Representation of the absorption spectra of liquid methyl cyanide and isocyanide in the photographic infra-red.

TABLE II

WAVE LENGTHS AND FREQUENCIES OF ABSORPTION MAXIMA OF METHYL CYANIDE AND METHYL ISOCYANIDE IN THE PHOTOGRAPHIC INFRA-RED

Methyl cyanide Vapor λ, Å.	Methyl cyanide Vapor ν, cm.$^{-1}$	Methyl cyanide Liquid λ, Å.	Methyl cyanide Liquid ν, cm.$^{-1}$	Methyl isocyanide Liquid λ, Å.	Methyl isocyanide Liquid ν, cm.$^{-1}$	Approximate description of band
		12373	8080	12560	7960	2ν(C—H) + ν(C≡N)
		12182	8206	12380	8075	
				12138	8236	3ν(C—H)
		12007	8326	11968	8353	
11727	8525	11767	8496	11800	8472	
11602	8617	11626	8598	11628	8597	
				11473	8714	
11360	8801	11405	8765	11327	8826	Possibly H_2O
(11238)	(8896)	11140	8974	11093	9012	
		10490	9530	10310	9697	?
		10145	9854	10157	9843	
		10037	9960	10008	9989	
		8973	11141	8937	11187	4ν (C—H)
		8922	11205	8898	11235	

It does not seem possible to identify all the maxima at present except in a very general way as done in the table. The complexity of the spectrum in the 8500 cm.$^{-1}$ region is presumably due to the partial removal of the degeneracy in the C–H vibrations in the higher levels.

Summary

A vibrational analysis is made of the spectra of methyl cyanide and methyl isocyanide. Evidence is given which indicates that although the carbon–nitrogen linkage in the isocyanide approaches rather closely to a triple bond it does possess an appreciable amount of double bond character. This, however, does not produce any deviation from linearity in the C—N≡C group and methyl isocyanide appears to possess a threefold axis of symmetry.

The absorption spectra of methyl isocyanide in the liquid state, and of methyl cyanide in the liquid and vapor states have been photographed in the photographic infra-red.

PASADENA, CALIF. RECEIVED NOVEMBER 27, 1936

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[9] Badger and Bauer, *J. Chem. Phys.*, **4**, 469 (1936).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

The Densities of Fine Powders

BY J. L. CULBERTSON AND ALVER DUNBAR

No little work has been done in recent years on the problem of the densities of fine powders and especially those powders having a porous structure. Cude and Hulett[1] found in determining the density of charcoal in carbon disulfide, water, benzene and carbon tetrachloride that the apparent density, as determined in the different liquids, decreased in the order named. From a study of their results the conclusion was reached that the density values varied due to different degrees of penetration of the porous microstructure of the powder by the different liquids, the degree of penetration being governed by the surface tension and the fluidity of the liquids. Harkins and Ewing[2] also working with active charcoal made density determinations in a number of liquids. A similar variability was obtained though not in entire agreement with Cude and Hulett. They concluded that a compression of the liquid film at the solid–liquid interface caused the apparent density of the powder to be abnormally high and that the liquids with the greatest compressibility gave to the powder the greatest density. Later Howard and Hulett[3] with new data opposed the theory of film compression. Lamb and Coolidge[4] studying the heats of adsorption of vapors on charcoal found that the data gave support to the theory of a compressed layer at the solid–liquid interface and M. W. Tschapek[5] indicated that his density measurements of several solids in water and benzene lead to the same conclusion.

It appeared to the writers that a reconsideration of the apparent densities of two solids of quite different character as measured in each of a group of liquids should give a better concept of the causes of their variations in value. To this end the densities of silica gel and an active charcoal were determined in each of four different liquids.

Materials

All materials were carefully prepared or purified. The solids used were silica gel and an active (practically ash free) charcoal. The liquids were water, benzene, carbon tetrachloride and petroleum ether. The best laboratory reagent quality of the organic liquids was selected and each of these was specially purified. The purification in each case was concluded with thorough treatment with dehydrating agents in order to ensure completely anhydrous liquids, phosphorus pentoxide being used with carbon tetrachloride and sodium with benzene and petroleum ether.

Silica gel was prepared by precipitation from sodium silicate solution with ferric chloride by the method of Holmes, Sullivan and Metcalf.[6] After drying, the gel was pulverized in a pebble mill and screened through a 200-mesh screen.

Carbon was prepared from a commercial active charcoal, the mineral content being removed by the method of E. J. Miller.[7] The final treatment was to heat to approximately 900° in a closed crucible for a period of two hours. Analysis of this product showed it to have an ash content of 0.02 ± 0.005%.

Procedure

The density determinations were made by enclosing 2 to 3 g. samples of the solid in Pyrex bulbs and evacuating the bulbs while their temperature was maintained at 475 ± 20°. After evacuation the bulbs were sealed off while still hot, cooled, weighed in air, and then the tip, at the point of sealing, broken off under the surface of a portion of the freshly degassed liquid. The bulb was then suspended in the liquid by means of a loop of fine platinum wire and weighed while immersed. After emptying the bulb, it was reweighed in the liquid and in air, the tip broken off when the bulb was opened being accounted for in the latter weighing. Calculation of the density may be summarized in the following formula, after Lowry[8]

$$S = \frac{A - B}{[(A - B) - (C - D)]/d}$$

where A = weight glass and sample in vacuum
B = weight glass in vacuum
C = weight glass and sample in the liquid

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(1) Cude and Hulett, THIS JOURNAL, **42**, 391–401 (1920).

(2) Harkins and Ewing, *ibid.*, **43**, 1787–1802 (1921).

(3) Howard and Hulett, *J. Phys. Chem.*, **28**, 1082–1095 (1924).

(4) Lamb and Coolidge, THIS JOURNAL, **42**, 1146–1170 (1920).

(5) Tschapek, *Kolloid. Z.*, **63**, 34–6 (1933).

(6) Holmes, Sullivan and Metcalf, *Ind. Eng. Chem.*, **18**, 386 (1926).

(7) Miller, *J. Phys. Chem.*, **30**, 1031 (1926).

(8) Lowry, THIS JOURNAL, **46**, 824 (1924).

D = weight glass in liquid
d = density of the liquid

The bulbs were evacuated by means of an oil pump. For the charcoal a period of eight to ten hours of evacuation was required and for the silica gel thirty-six to forty hours. Not having available a McLeod gage, the exact air pressure in the bulbs was not known, yet these periods were found to be of sufficient length that longer evacuation yielded no appreciable change in the density values. The final weighings of the sample suspended in the liquid were made approximately two hours after the sample was wetted. This procedure does not eliminate all the effect of the drift discussed by Cude and Hulett,[1] but from an inspection of the curves presented by these authors and from the reproducibility of the results found in the present investigation when weighings were made from one and one-half to two and one-half hours after wetting, it was concluded that the method adopted yielded values that might be confidently used for purposes of comparison.

Results and Discussion

The values of the densities of the active charcoal and silica gel in each of the four liquids are presented in Table I.

TABLE I

APPARENT DENSITIES OF CHARCOAL AND SILICA GEL AT 25°

	Charcoal, g./cc.	Silica gel, g./cc.
Water	1.821	2.246
Benzene	1.994	2.149
Carbon tetrachloride	1.860	2.132
Petroleum ether	2.083	2.125

It is interesting to note that in this restricted group, water, the liquid which yields the highest density for silica, yields the lowest density for charcoal, while the petroleum ether which yields the highest density for charcoal yields the lowest density for silica. It is the special purpose of this paper to point out this fact and to consider its consequences. The same sort of inverted relationship is seen between water and benzene, benzene and petroleum ether, water and carbon tetrachloride, carbon tetrachloride and petroleum ether but not between benzene and carbon tetrachloride. It should be stated immediately, however, that this inverted relationship is not as general as is indicated by the data from this group of liquids. Further work in this Laboratory[9] with other liquids develops such a point but the argument presented below is proposed with this fact in mind and is in no sense invalidated by it. In this series it is quite possible that the benzene–carbon tetrachloride relationship is affected by an abnormal condition of the charcoal–carbon tetrachloride system. This is suggested by the work of Pearce[10] who concluded that some decomposition of the carbon tetrachloride occurred at the charcoal surface and also, for the reasons discussed below, by his observation that the heats of adsorption of the chlorine substituted methanes increased with increased chlorine content up to the tri-substituted compound, then dropped off for the tetrachloride.

It is obvious that an adequate theory of the differences in the apparent density of a solid as indicated by different liquids must harmonize with the situation presented by the above data. This point is strengthened by the fact that the results are in good agreement with the values obtained for charcoal in most of the investigations noted above and for silica in the work of Tschapek.[5]

A consideration of the theories presented by the other workers, however, in the light of the values for the two solids, reveals certain elements of inconsistency. If the liquids penetrated the microstructure of the solids to different degrees as a result of differences in molecular size, fluidity or surface tension of the liquids themselves, it would be impossible for the situation indicated by these data to obtain: *e. g.*, high density of silica in water and low density of carbon in the same liquid. It is equally true that if the compressibility of the liquids were the sole factor involved then the observed data would hardly be explicable.

It appears to the writers that the mutual relation between liquid and solid at the interface must be of vital importance. Of all the highly porous insoluble powders readily obtained, charcoal seems to be more organophilic in nature than any other. This statement very probably will have a surer foundation if we limit it to the organic compounds of non-polar type. On the other hand, the silica gel is distinctly hydrophilic. The tentative hypothesis would be offered then that the observed variations in density are due to one or the other of the following factors: first, differences in the degree of penetration of the porous solid by the liquids as a result of differences

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(9) Culbertson and Weber, unpublished data.

(10) Pearce, *J. Phys. Chem.*, **34**, 1260–1279 (1930).

in the surface energy decrease on wetting; or second, differences in the degree of compression of the liquids at the solid–liquid interface as determined, primarily, by the different forces of attraction at the interfaces and, secondarily, by the different compressibilities of the liquids. The results obtained as yet are such that either or both of these factors may be of significance. In case the liquid compression is dominant it is clear that the interfacial force or energy relations are of greater importance than the actual compressibilities of the liquids, for the reason mentioned above in connection with the compression theory. Either of the above postulates requires an intimate relation between density values and the decreases in surface energy when the solid is wetted by the liquids. The complexity of the situation, however, involving the unknown specific areas of the solids used and the possible subordinate role of the compressibilities of the liquids, renders the quantitative treatment of this relation yet impossible. A comparison of the order in which the density values fall, however, with some data on other interfacial phenomena such as adhesion tensions[11] and heats of wetting,[12] shows a rather striking similarity which seems to offer strong support for the postulates advanced.

Summary

Measurements of the apparent densities of charcoal and silica gel in water, carbon tetrachloride, benzene and petroleum ether have been made. The liquids, water and petroleum ether, which, respectively, show the highest and lowest apparent densities for silica yield values of the opposite order for charcoal. Some existing theories are examined in the light of the data found and a new postulate advanced.

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[11] Bartell and Osterhoff, *J. Phys. Chem.*, **37**, 543 (1933).

[12] Patrick and Grimm, This Journal, **43**, 2144–2150 (1921); Bartell and Almy, *J. Phys. Chem.*, **36**, 985–999 (1932); Andress and Berl, *Z. physik. Chem.*, **122**, 81–86 (1926); Culbertson and Winter, unpublished data.

Pullman, Wash. Received October 6, 1936

[Contribution from the Laboratory of Physical Chemistry, The State College of Washington]

Heats of Wetting of Activated Charcoal and Silica

By J. L. Culbertson and L. L. Winter

The results of a recent investigation in this Laboratory[1] on the apparent densities of active charcoal and silica gel, when various liquids were used as the buoying fluids, led to the suggestion that a significant relation existed between the density values and the interfacial energy changes when the solids were wetted by the liquids. In particular it was pointed out that when the apparent density values as found by immersion in the different liquids were arranged in increasing or decreasing order, then the corresponding values of the heats of wetting of similar solids by the liquids, as recorded by a number of investigators, were found in most cases to be in the same order. Since, in the investigation referred to, a considerable quantity of both the active charcoal and silica gel had been prepared, it was considered an excellent opportunity to study the heat of wetting characteristics of the solids when samples were available which were identical in all respects with the material used in the density determinations. In making these latter determinations the samples had been enclosed in glass bulbs and evacuated at elevated temperatures before immersion. It was decided therefore that, though in most of the studies of heats of wetting found in the literature non-evacuated samples were used, a technique must be adopted which would put the solid in approximately the same condition as it had been in the density measurements.

To accomplish this end the samples were enclosed in specially designed glass bulbs and evacuated at 220° for thirty-six hours by means of an oil pump. After sealing off the bulbs while still hot, the latter were cooled and weighed. Wetting of the sample in the calorimeter was accomplished by crushing the bulb, a mechanism being employed which permitted this to be accomplished without opening the calorimeter. This mechanism consisted of a steel holder so arranged that a screw, projecting through the calorimeter closure and operated by hand, compressed the bulb supports. A one-liter Dewar cylindrical flask closed with a thick tightly fitting cork served as the calorimeter. This was set in a water-bath main-

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[1] Culbertson and Dunbar, This Journal, **59**, 306 (1937).

tained at 25 ± 0.1°. A motor-driven stirrer operated in the calorimeter throughout a determination and the heat capacity of the entire assembly was determined immediately after each run. This was accomplished by means of a measured amount of electrical energy introduced through a resistance wire. Temperature differences were read from a Beckmann thermometer.

Materials.—In the previous investigation referred to, four liquids had been used in determining the densities of the solids. These were water, benzene, carbon tetrachloride and petroleum ether. For the present work these were used and were prepared in the same way as in the previous study. In addition, two other liquids were prepared and used, nitrobenzene and carbon disulfide. The nitrobenzene was treated with sodium hydroxide, washed with water, and dried with calcium chloride. It was then distilled three times, a constant boiling middle portion being secured. The carbon disulfide was treated with mercury and with mercuric chloride, washed with water and dried with phosphorus pentoxide. It was then distilled three times as was the nitrobenzene. The solids, charcoal and silica gel, were portions of the same materials as were used in the density determinations and their preparation has been described in the report of that work.

Results and Discussion.—The values obtained for the heats of wetting of the two solids by the various liquids are indicated in Table I. Three values for each case show the order of agreement in duplicate determinations.

TABLE I

HEATS OF WETTING OF SILICA AND CHARCOAL

Liquid	$-\Delta H$ on silica, cal./g.	$-\Delta H$ on charcoal, cal./g.
Water	16.0	8.5
	16.2	8.5
	15.9	8.3
Average	16.0	8.4
Nitrobenzene	14.3	27.1
	14.5	27.2
	14.2	27.0
Average	14.3	27.1
Benzene	10.9	20.8
	11.4	21.2
	11.2	21.2
Average	11.2	21.0
Carbon disulfide	6.5	29.2
	6.7	29.6
	6.8	29.6
Average	6.7	29.5
Carbon tetrachloride	6.1	19.7
	6.3	20.1
	6.5	20.2
Average	6.3	20.0
Petroleum ether	4.1	23.7
	4.3	23.9
	4.5	23.8
Average	4.3	23.8

In general it may be said that the heats of wetting of silica gel agree well with those found by Berthon,[2] Patrick and Grimm,[3] and Bartell and Fu,[4] though somewhat greater differences between the values for the organic liquids are observed. With the charcoal the agreement with other workers is not so close due no doubt to the wide variations in charcoal used by different investigators. It is believed by the writers that these data represent very reliable values for the systems named because of the care used in evacuating the samples and also because of the fact that in the case of the charcoal, virtually ash free samples were used. The latter point seems especially significant for in view of the relationship between the heats of wetting of the water and the organic liquids on silica it appears that even a moderate percentage of mineral content in the charcoal would alter entirely the heat of wetting relationship. This is well substantiated by a glance at the tables of the "I. C. T."

Of especial interest is the fact that water with the highest heat of wetting on silica yields the lowest value on charcoal. It is also noteworthy that the petroleum ether, exhibiting the lowest heat change with silica, shows a high, though not the highest in the group, heat of wetting on charcoal. Qualitatively these relationships show clearly that the two fundamentally different types of solids, silica and charcoal, possess quite different energy change characteristics when wetted by liquids. In broad terms this is summed up in the statement that the charcoal undergoes a high energy change at the solid–liquid interface when wetted by organic liquids and relatively low change when wetted by water. The exactly opposite situation is obtained in the case of the silica gel. In more detail, however, it is to be noted that nitrobenzene appears in second place in each column. This probably may be interpreted to mean that on silica the polar nitro group is oriented to the solid surface while on the

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(2) Berthon, *Compt. rend.*, **195**, 1019–1021 (1932).

(3) Patrick and Grimm, THIS JOURNAL, **43**, 2144–2150 (1921).

(4) Bartell and Fu, "Colloid Symposium Annual," **7**, 135–149 (1929).

carbon the orientation is in the opposite direction, though why the latter should show such an increased heat of wetting over that of benzene is not obvious.

In the previous work on the densities of these solids a correlation with existing data on heats of wetting is mentioned. How well this is borne out in the present work is indicated in Table II.

TABLE II

DENSITIES AND HEATS OF WETTING OF SILICA GEL AND CHARCOAL

Liquid	Silica: Heat of wetting, cal./g.	Silica: Density, g./cc.	Charcoal: Heat of wetting, cal./g.	Charcoal: Density, g./cc.
Water	16	2.25[a]	8.4	1.82
Nitrobenzene	14.3	2.23	27.1	2.00[a]
Benzene	11.2	2.15	21.0	1.99
Carbon disulfide	6.7	2.21[a]	29.5	2.02[a]
Carbon tetrachloride	6.3	2.13	20.0	1.86
Petroleum ether	4.3	2.12	23.8	2.08

[a] The values so indicated are due to Culbertson and Weber (unpublished data). Identical silica gel and charcoal were used but the method of Tschapek [*Kolloid. Z.*, **63**, 34–36 (1933)] was employed in making the determinations. This method was compared with that used by Culbertson and Dunbar and satisfactory checks were obtained.

For the most part high heats of wetting accompany high densities though carbon disulfide on silica appears to provide an exception to such a generalization. It is the contention of the writers, however, that such evidence as these data afford tends to confirm the ideas expressed in the paper by Culbertson and Dunbar,[1] *e. g.*, that differences in the apparent density of a porous solid as indicated by measurements made with different liquids as filling fluids are due either to differences of penetration of the pores of the solid by the liquids or to differences in the amount of compression of the liquid film at the interface, in either case the determining factor being the decrease in surface energy when the liquid wets the solid. Quantitative correlation is of course lacking in Table II, but in consideration of the fact that if the above view of these phenomena is correct, then the specific areas of the solids, the compressibilities and the heats of compression of the different liquids, satisfactory data for most of which are unavailable, would have to be taken into consideration in developing such quantitative ideas and therefore the irregularities found are quite within the expected magnitude.

Summary

The heats of wetting of charcoal and silica gel by water, nitrobenzene, benzene, carbon tetrachloride, carbon disulfide and petroleum ether have been determined. A correlation is noted between the order in which these values fall and that of the apparent densities of the solids as determined in the same liquids.

PULLMAN, WASH. RECEIVED OCTOBER 6, 1936

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Accumulation of Alkali Promoters on Surfaces of Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND S. BRUNAUER

It has been pointed out repeatedly that the high pressure activity of iron synthetic ammonia catalysts containing a per cent. or so of potassium oxide in addition to an approximately similar amount of aluminum oxide is considerably greater than that of a catalyst promoted with aluminum oxide alone.[1] So far as we are aware, however, no evidence has ever been published concerning the fraction of the catalyst surface actually covered by the few per cent. of the alkali oxide promoters contained in typical iron synthetic ammonia catalysts. It is the purpose of the present paper to show that some recently determined low temperature adsorption isotherms of nitrogen, carbon monoxide and carbon dioxide on five different synthetic ammonia catalysts, enable us to conclude that 1% or so of potassium oxide in a catalyst actually covers a large fraction of the catalyst surface.

Experimental

The adsorption apparatus used was similar to that already described[2] except that parts F, E, C′, C, M, A, N, L, K, J and trap H of the apparatus shown in Fig. 1 of that paper were eliminated, and a manometer made of 10-mm. tubing was attached at the top of buret B. Stopcocks 1 and 2 were replaced by mercury sealed vacuum cocks, and catalyst bulb A was replaced by one of 25-cc. capacity.

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[1] Larson, *J. Ind. Eng. Chem.*, **16**, 1002 (1924); Almquist and Crittenden, *ibid.*, **18**, 1307 (1926).

[2] Emmett and Brunauer, THIS JOURNAL, **56**, 35 (1934).

The Toepler pump used in some of the experiments was attached essentially as shown in Fig. 1 of the above paper.

The iron synthetic ammonia catalysts were samples that had been prepared as oxides about ten years previously by the fusion method of Larson and Richardson[3] and kept in stoppered bottles since that time. According to their procedure, the promoters (pure potassium nitrate and Norton R. R. Alundum) were incorporated into the fused oxides at about 1540°. The catalyst composition, weight, reduction schedule and activity toward the high pressure synthesis of ammonia are presented in Table I for each of the five different types of synthetic ammonia catalysts used.

TABLE I

Mesh size, 8 to 14. Apparent volume of catalysts, 25 cc. Hydrogen flow during reduction, 500 cc. per min.

Catalyst	Sample as oxide, g.	Promoter content, %	Reduction schedule Time, hrs. Temp., °C.	Activity[a] toward ammonia synthesis (% NH_3 at 450°, 100 atm. and 5000 space velocity)
930	64.5	1.07 K_2O	48 between 350 and 450	5.3
931	61.0	1.59 K_2O 1.3 Al_2O_3	18 at 300 to 350 65 more 350–450 18 more 450–530	12.3
954	66.8	10.2 Al_2O_3	48 at 350 to 450 48 more at 450–500	8.2
958	71.9	0.35 Al_2O_3 .08 K_2O	36 at 350 to 450 36 more at 450–500	10.4
973–I	63.4	.15 Al_2O_3	124 at 300 to 350 54 more at 375–500	3.3
973–II	67.0	.15 Al_2O_3	96 at 300 to 400	

[a] The high pressure activities given here were determined about ten years ago on other samples of these same catalysts. They are included in this table merely as illustrations of the approximate relative activities of the various catalysts.

Hydrogen from large electrolytic cells in operation at this Laboratory was used after being passed over hot copper and dried by phosphorus pentoxide. All copper purifiers were first heated in hydrogen for several hours at 750° to remove traces of sulfur that might be present. Tank nitrogen was passed slowly over hot copper and dried by passage over phosphorus pentoxide. Carbon monoxide prepared according to the method of Thompson[4] was taken from tanks and passed through liquid air traps to remove iron carbonyl and any traces of carbon dioxide. Tank carbon dioxide was dried by passage through a trap immersed in an alcohol–dry ice bath at −78° and was used without further purification after it had been shown to contain only a negligible amount of non-condensable gases.

The liquid oxygen used as a constant temperature bath was prepared immediately before use by passing tank oxygen into a condenser cooled in liquid air. The only two tanks of the oxygen analyzed contained 2.0 and 3.4% nitrogen; oxygen liquefied from the latter of these two tanks was found to retain 0.9% nitrogen. The Dewar flask used as a container for the liquid oxygen during the adsorption experiments was not silvered and permitted rapid evaporation of oxygen. Apparently quite a constant temperature was obtained during a given run, the temperature change during the day being less than 0.05° as judged by a ten-junction copper–constantan thermocouple used in conjunction with a type K potentiometer. The temperature of the cold bath was obtained by noting the barometric pressure and using the tables of Dodge and Davis[5] for the vapor pressures of liquid oxygen. The temperature of −78.5° was obtained by using an alcohol–dry ice bath stirred only by the bubbling caused by the gradual evaporation of carbon dioxide. It is realized that such a bath might have been a degree or so warmer at the top than at the bottom, though the temperature at the bottom of the bath opposite the catalyst bulb was close to −78.5° as indicated by a calibrated thermocouple and a pentane thermometer. The adsorption measurements were carried out in the usual fashion, helium[6] calibrations of the dead space in the catalyst bulb being made before each series of runs. The catalyst was always first cooled in helium to the desired low temperature before admitting either carbon monoxide or carbon dioxide. After sufficient time had been permitted for temperature equilibration between the catalyst and the surrounding bath the helium was removed and the catalyst evacuated to about 10^{-4} mm. immediately before each run. To avoid the possibility of traces of oxygen contaminating the catalyst overnight, a uniform reduction period of one hour, in a stream of about 500 cc. of hydrogen per minute, was carried out every morning at 450°.

The gas contained in the "dead space" around the catalyst was corrected in each case for deviations from the perfect gas laws with the help of data from the "International Critical Tables." The corrections used were 3.2% for carbon monoxide at −183°, 2.97% for nitrogen at −183°, 2.0% for carbon dioxide at −78.5° and 0.58% for carbon dioxide at room temperature. Values for the first three of these corrections were also obtained through the kindness of Dr. A. F. Benton from some measurements that he and his collaborators have made recently. His results are in substantial agreement with the above corrections.

Results and Discussion

The carbon dioxide adsorption on the various iron catalysts at −78.5° was found to have many of the characteristics to be expected for a purely physical type of adsorption. For example, the rate of adsorption is rapid at all pressures; furthermore, it is no slower for catalysts promoted with alkalies than for those promoted with aluminum oxide alone. However, even a cursory comparison of the adsorption isotherms for carbon dioxide and for nitrogen shows that the ratio of the volume of carbon dioxide capable of being adsorbed at −78.5° to the volume of nitrogen that can be adsorbed at −183° on the same catalyst is

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(3) Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

(4) Thompson, *ibid.*, **21**, 389 (1929).

(5) Dodge and Davis, THIS JOURNAL, **49**, 610 (1927).

(6) We wish to express our thanks to Dr. R. Wiebe of this Laboratory for furnishing us a supply of helium that he had purified by passing through charcoal tubes immersed in liquid air. His analysis by use of an interferometer showed that the helium was 99.94% pure.

much higher on a catalyst promoted with alkali than on one to which no alkali has been added.

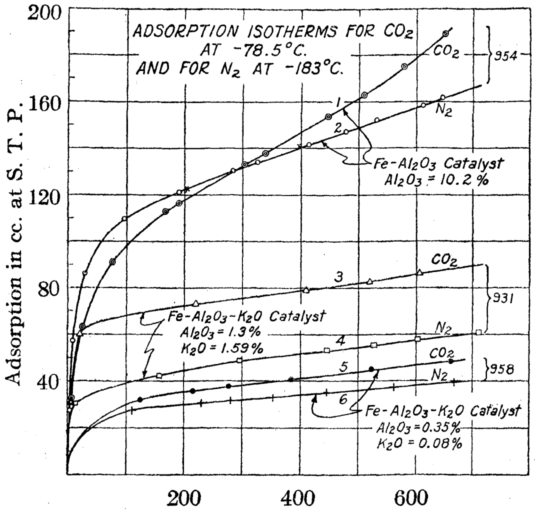

Fig. 1.—Comparison of the adsorption isotherm for carbon dioxide at −78.5° on a given iron synthetic ammonia catalyst with that for nitrogen at −183° on the same catalyst.

Figures 1 and 2 afford such a comparison between the isotherms of carbon dioxide at −78° and nitrogen at −183°, for the various catalysts. It is evident that at 300 mm. pressure[7] the volume of carbon dioxide adsorbed by catalyst 954 (10.2% Al_2O_3) at −78.5° is exactly the same as the volume of nitrogen adsorbed at −183°. On the other hand, at this same pressure in the case of catalysts 930, 931 and 958, which as pointed out above contain 1.07, 1.59 and 0.08% K_2O, respectively, the carbon dioxide isotherms at −78.5° exceed those for nitrogen at −183° by 78, 55 and 20%. For catalyst 973, to which no promoter had been added, the carbon dioxide adsorption for sample II is 10% larger at 300 mm. than the nitrogen adsorption at −183° and for sample I, 8% larger. In view of the marked influence of 0.08% K_2O in catalyst 958 on the total carbon dioxide adsorption it seems probable that the results on "pure iron" catalyst 973 may actually indicate the presence of a few hundredths of a per cent. of alkali even though none was intentionally added. Presumably, then, something other than the physical adsorption of carbon dioxide was occurring on the alkali-promoted catalysts at −78.5°.

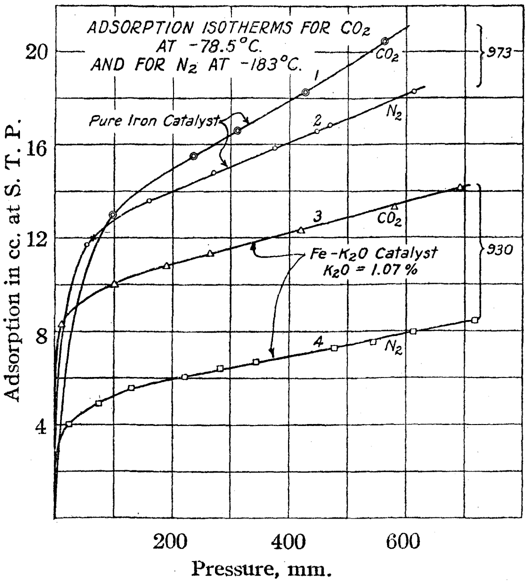

Fig. 2.—Comparison of the adsorption isotherm for carbon dioxide at −78.5° on a given iron synthetic ammonia catalyst with that for nitrogen at −183° on the same catalyst.

A reasonable interpretation of the large excess of carbon dioxide taken up by the catalysts containing potassium oxide appeared to be that the surface alkali was causing a very rapid[8] chemisorption of carbon dioxide to occur in addition to about the usual amount of physical adsorption. To obtain further evidence regarding the existence of such chemisorption and to ascertain the approximate amount of it that might be occurring, the catalysts were degassed by a diffusion pump for thirty minutes at 0° at the end of an isotherm determination, in order to remove the physically adsorbed carbon dioxide, after which the −78.5° isotherms were repeated. The slopes of the straight line portion of these second isotherms were in all cases practically the same as the slopes of the carbon dioxide isotherms shown in Figs. 1 and 2. However, the actual amount of adsorption occurring at −78.5° following the evacuation at 0° was smaller than the original carbon dioxide adsorption by 5 cc. for catalyst 954, 30 cc. for catalyst 931, 8 cc. for catalyst 958, 4.2 cc. for catalyst 930 and 2 cc. for catalyst 973. (For the

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(7) 300 mm. was arbitrarily chosen as the pressure at which to make this comparison between catalysts promoted with alkali and those to which no alkali had been added. Any pressure in the range in which sufficient observations had been made to fix the shapes of the isotherms (roughly 100 to 700 mm.) would have served equally well.

(8) Only a few desorption points were taken on the runs with carbon dioxide at −78.5°. They showed, however, that on catalyst 931 at least 93% and possibly all of the chemisorption of carbon dioxide occurring during an entire isotherm determination had completed itself in the first fifteen minutes of the run and at a pressure of 25 mm. or less.

original carbon dioxide adsorption values see the curves in Figs. 1 and 2.) These values for the decreases in adsorption following the evacuation at 0° correspond to 67, 62 and 25% of the −183° nitrogen isotherm adsorption values at 300 mm. for the alkali-containing catalysts 930, 931 and 958, but only 4.7 and 13.5% in the case of catalysts 954 and 973 to which no alkali had been added. A comparison of these percentages with those given in the previous paragraph shows clearly that the volume of carbon dioxide that is rapidly adsorbed at −78.5° but not removed from the catalysts upon half an hour of evacuation at 0° is about sufficient to account for the amounts by which the total carbon dioxide adsorptions at −78.5° on the alkali-containing catalysts exceed the nitrogen adsorption at −183° and 300 mm. pressure. There seems to be little doubt, accordingly, that a considerable portion of the carbon dioxide adsorbed by the catalysts containing alkali is actually held to the catalyst by a process of chemisorption rather than physical adsorption.

An exact determination of the amount of chemisorption of carbon dioxide occurring on the various catalysts could be made only in case some temperature could be found at which all of the van der Waals adsorption would be removed by evacuation without any of the chemisorption being removed. If it could be shown, for example, that evacuation at 100° for a half hour removed none of the carbon dioxide that could not be removed by a similar period of evacuation at 0°, then the numerical values previously found for the differences between the initial total carbon dioxide adsorptions and the adsorptions following an evacuation at 0° would be considered correct values for the chemisorption of carbon dioxide at −78.5° on the various catalysts. This indeed proved accurately to be the case for most of the catalysts studied. Thus, three and one-half hours of evacuation of catalyst 931 at 0° removed no more carbon dioxide than had been removed in half an hour. Furthermore, pumping at 100° for half an hour removed no greater amounts of carbon dioxide from this catalyst or from catalysts 954 or 930 and only 0.2 cc. more from catalyst 973 than had been removed at 0°. Only from catalyst 958 did it appear possible by pumping at 100° to remove considerable carbon dioxide that could not be removed by pumping for a similar period at 0°. In this instance evacuation at 0° left 8 cc. of carbon dioxide on the surface whereas two 100° evacuations in separate runs left 7.1 and 5.0 cc. of carbon dioxide on the catalyst. Accordingly, one can merely say that out of the total carbon dioxide adsorption shown by curve 5, Fig. 1 (catalyst 958), between 5 cc. and 8 cc. is chemisorption. It may be of interest to point out that evacuation of catalyst 931 with a diffusion pump for thirty minutes at as high a temperature as 450° removed only about one-half the carbon dioxide that could not be removed at 0°. Analysis of the first 2 or 3 cc. of gas coming off the catalyst at 450° indicated the presence of both carbon monoxide and carbon dioxide, the latter predominating. The carbon monoxide probably came from the reaction of carbon dioxide with the iron atoms of the catalyst surface. It appears, therefore, that the chemisorbed carbon dioxide is very tightly bound to the catalyst surfaces containing alkali.

No definite evidence exists in the present work as to the number of carbon dioxide molecules that are chemisorbed on the catalysts by each alkali molecule on the catalyst surface. Neither is there any information concerning the nature of the surface alkali though presumably it cannot be present as potassium atoms since Brewer[9] has shown by photoelectric experiments that the concentration of free potassium atoms on the surface of promoted iron synthetic ammonia catalysts is very small. It seems probable that the alkali concerned in the chemisorption of carbon dioxide in the present experiments is in the form of an oxide or a complex with iron or iron oxide. By making the plausible assumption that each alkali molecule present on the surface of the catalyst is capable of holding one molecule of chemisorbed carbon dioxide, and by taking into account the amount of carbon dioxide needed to form a monolayer of physical adsorption on the catalyst as a whole, one is led inevitably to the conclusion that during the preparation or reduction of the catalyst alkali has accumulated to a marked extent on the catalyst surface. In fact, on the basis of our best estimates of the surface area[10] the alkali covers about 71 and 75% of the surface of catalysts 930 and 931, respectively, although the

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[9] Brewer, THIS JOURNAL, **53**, 74 (1931).

[10] The principle of the method used in measuring the surface areas has already been presented [see Brunauer and Emmett, *ibid.*, **57**, 1754 (1935)]. A detailed discussion of the method with its application to a number of synthetic ammonia catalysts and other catalytic substances will soon be submitted for publication. The estimates of the surface areas used in the present paper are based on the final revised estimates of the surface areas resulting from this more comprehensive work.

alkali contents of these two catalysts as a whole are only 1.07[11] and 1.59%.

A fortunate characteristic of the adsorption of carbon monoxide on iron catalysts at −183° enabled us to obtain evidence regarding the fraction of the total surface that consists of iron atoms rather than alkali molecules and to confirm thereby the above conclusions in regard to the accumulation of alkali on the catalyst surface. Early in the work upon the determination of catalyst surface areas by the use of low temperature isotherms it was noted that on pure iron catalyst 973 (Sample I) the carbon monoxide adsorptions were roughly twice as large as the nitrogen adsorptions at the same temperature and pressure, although the carbon monoxide adsorption equilibrated as rapidly as that of nitrogen. To ascertain whether chemisorption of carbon monoxide was occurring the catalyst was evacuated by a diffusion pump at temperatures up to −78° immediately following a run at −183°. Carbon monoxide adsorption isotherms made at −183° immediately following this evacuation at −78° showed an amount of physical adsorption of carbon monoxide comparable to that of nitrogen at −183°. It was therefore concluded that on the iron catalyst at −183° a practically instantaneous chemisorption of carbon monoxide was occurring which could not be removed by pumping for half an hour with a diffusion pump at −78°. Furthermore, the fact that this chemisorption reached a saturation value instantaneously at pressures of only a few mm. of carbon monoxide and did not continue during the subsequent determination of the superimposed physical adsorption up to 760 mm. led us to believe that at −183° a complete monolayer of chemisorbed carbon monoxide was formed on the catalyst surface.

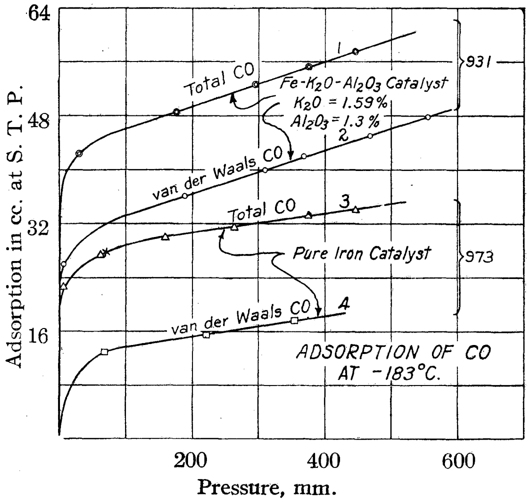

Fig. 3.—Comparison of the total carbon monoxide adsorption at −183° with the van der Waals adsorption for doubly promoted catalyst 931 and for pure iron catalyst 973. The X on curve 3 represents a desorption point.

If the chemisorption of carbon monoxide takes place on the iron atoms on the surface, then it should follow that the same catalysts that are capable of large chemisorptions of carbon dioxide should have low chemisorptions of carbon monoxide and *vice versa*. In Fig. 3 are presented curves showing the total adsorption and the van der Waals adsorption of carbon monoxide on a doubly promoted catalyst compared with an unpromoted catalyst. The isotherms designated as "van der Waals CO" were obtained at −183° immediately after determining the "total CO" isotherms at −183° and then evacuating the catalyst with a diffusion pump for a half hour at −78°. The difference between the two curves may be taken as the amount of chemisorbed carbon monoxide in each case because, as mentioned above, it was found that the chemisorbed carbon monoxide could not be removed by pumping at −78°. It is apparent that the doubly promoted catalyst, which had a large carbon dioxide chemisorption, has a small carbon monoxide chemisorption, whereas the pure iron catalyst with little or no chemisorption of carbon dioxide has large carbon monoxide chemisorption. The carbon dioxide and carbon monoxide chemisorptions therefore each leads independently to the conclusion that the 1 or 2% K_2O present in promoted iron synthetic ammonia catalysts covers a large fraction of the surface of the catalyst.

Throughout the present paper we have generally referred to the irreversible carbon monoxide and carbon dioxide adsorptions as chemisorptions. At present we do not wish to enter into an extended discussion in regard to the most appropriate nomenclature for sorptions of a chemi-

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(11) In the course of the reduction of catalyst 930 the glass adsorption bulb became heavily frosted, presumably due to the volatilization of alkali from the catalyst. Analysis of the alkali on two of these frosted catalyst bulbs showed that 65 and 54%, respectively, of the 1.07% alkali had volatilized onto the glass. Hence, the alkali remaining in the catalyst was only 0.4 to 0.5% in all the runs on catalyst 930 rather than the 1.07% reported in the present paper. It was also shown by a blank run on a third such catalyst bulb from which the catalyst had been removed immediately after reduction that no carbon dioxide (less than 0.1 cc.) was taken up at −78° by the alkali on the glass. Any chemisorbed carbon dioxide reported in the present paper was therefore adsorbed by the catalyst or by the alkali on the catalyst and not by the alkali on the glass reaction vessel.

cal type. In those instances in which a surface adsorption can be shown to be a slow surface process whose rate is very sensitive to temperature, the name "activated adsorption" suggested by Taylor[12] is certainly descriptive and therefore appears to serve a useful purpose. However, in the present instances, the irreversible adsorptions of carbon monoxide on the iron catalysts and of carbon dioxide on the alkali promoted iron catalysts were not slow processes; they appear to be about as rapid as the accompanying van der Waals adsorption. The name "chemical adsorption" or "chemisorption" which has been used frequently in the past therefore appears to be a more descriptive one to apply to the present examples in order to emphasize their rather unique adsorption characteristics.

An accurate assessing of the present work as a contribution to a better understanding of the action of promoters in iron synthetic ammonia catalysts seems desirable at this point. Almquist[13] summarized the ways in which promoters may affect the activity of a catalyst by pointing out that they may serve either (1) to maintain a large surface area by retarding the growth of crystals in the catalysts, or (2) to change the qualitative nature of the surface by furnishing a promoter-catalyst interface that is more active as a catalyst than the same surface area of the pure catalyst. Furthermore, from the results of Almquist and Black,[14] as well as from previous work by Wyckoff and Crittenden,[15] it may be concluded that in the case of iron synthetic ammonia catalysts aluminum oxide alone, or aluminum oxide together with potassium oxide function in part at least in the first of these two ways. Recently determined[2] adsorption isotherms for nitrogen at −183° confirm this view by showing that catalysts promoted with either aluminum oxide or a combination of potassium oxide and aluminum oxide have much larger surfaces than have pure iron catalysts; however, they also show that a typical doubly promoted catalyst containing both potassium oxide and aluminum oxide has only about one-third as much surface as a catalyst promoted with aluminum oxide alone, even though the former is much more active at high pressures than the latter. It therefore seems very probable that an alkali such as potassium oxide, when added as a promoter to an iron catalyst together with a per cent. or so of aluminum oxide functions predominantly in the second of the two ways mentioned above, namely, by changing the qualitative nature of the catalyst surface. The present work, by indicating that about 70% of the surface of a doubly promoted catalyst is covered with alkali, brings to light the fact that only about one-third as much iron but about forty times as much alkali goes to make up the surface of a doubly promoted catalyst as one would have had reason to suspect heretofore. The precise mechanism through which the alkali when present with aluminum oxide so radically increases the activity of the surface per unit area is still a matter of conjecture and is not revealed by the present work.

Adsorption isotherms at −183° previously reported by Benton and White[16] for a sample of the same pure iron catalyst (973) as used in some of the present experiments agree qualitatively with our results in indicating that the total adsorption of carbon monoxide at −183° is much larger than that of nitrogen at −183°. However, their adsorption of carbon monoxide at −183° is only about 40% larger than that of nitrogen, whereas our results yield a total carbon monoxide adsorption that is consistently at least 100% larger than that of nitrogen. No explanation of this discrepancy between their results and ours is evident at this time.

Summary

With the help of adsorption isotherms for carbon monoxide and nitrogen at −183° and for carbon dioxide at −78.5° evidence has been obtained to show that a per cent. or so of potassium oxide in an iron synthetic ammonia catalyst actually covers more than 50% of the total surface of the catalyst. Apparently at −183° carbon monoxide rapidly forms a monolayer of chemisorbed carbon monoxide on the iron atoms of the catalyst, whereas at −78.5° carbon dioxide rapidly forms a layer of chemisorbed carbon dioxide on that portion of the surface that is covered by alkali.

WASHINGTON, D. C. RECEIVED NOVEMBER 21, 1936

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[12] Taylor, THIS JOURNAL, **53**, 578 (1931).

[13] Almquist, *ibid.*, **48**, 2820 (1926).

[14] Almquist and Black, *ibid.*, **48**, 2814 (1926).

[15] Wyckoff and Crittenden, *ibid.*, **47**, 2866 (1925).

[16] Benton and White, *ibid.*, **54**, 1806 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Equilibrium between Nitric Oxide, Nitrogen Peroxide and Aqueous Solutions of Nitric Acid

BY F. S. CHAMBERS, JR., AND T. K. SHERWOOD

The absorption of nitrogen oxides by water to produce nitric acid involves the principal reactions

$$2NO + O_2 = 2NO_2 \rightleftarrows N_2O_4 \qquad (1)$$

$$3NO_2 + H_2O = 2HNO_3 + NO \qquad (2)$$

The first proceeds slowly and probably determines the rate of nitric acid formation in dilute solution. The importance of the readily displaceable equilibrium (2) was first pointed out by Burdick and Freed,[1] who were able to give a rational explanation of the relatively low nitric acid strengths obtainable on the absorption by water of gases produced by the oxidation of ammonia.

Burdick and Freed also reported data on the equilibrium for the second reaction, expressing their results in the form of the equilibrium constant

$$K = \frac{(P_{NO})\,(P_{HNO_3})^2}{(P_{NO_2})^3\,(P_{H_2O})}$$

which they considered to be the product of the two parts

$$K_1 = \frac{(P_{NO})}{(P_{NO_2})^3} \qquad K_2 = \frac{(P_{HNO_3})^2}{(P_{H_2O})}$$

Determinations of the gas compositions in equilibrium with aqueous solutions of nitric acid led to values of K_1 for various acid strengths for temperatures from 10 to 75°. Separate determinations of the vapor pressures of water and of nitric acid over similar solutions led to values of K_2 covering a similar range. Since the publication of their results Taylor[2] has presented a summary of the available vapor pressure data, from which values of K_2 may be calculated.

More recently Abel, Schmid and Stein[3] have studied the equilibrium of reaction (2) and report values of K differing by roughly 10-fold from those of Burdick and Freed. From 35 to 60% nitric acid the discrepancy is relatively constant, the values of K reported by Abel, Schmid and Stein being about five times those of Burdick and Freed. At lower acid strengths the discrepancy is in the same direction but much greater. At low acid strengths, however, the accuracy is poor because of the difficulty of measuring the corresponding low pressures of nitrogen peroxide. Since this pressure enters as the third power in K_1 any errors in its measurement become greatly magnified.

The discrepancies between the results of Burdick and Freed and of Abel, Schmid and Stein suggested the present attempt to measure the equilibrium by a new method. Since the solution activities used[4] by Abel, Schmid and Stein in evaluating K_2 were consistent with the vapor pressure determinations of Burdick and Freed and with the correlation of vapor pressure data given by Taylor, it seemed clear that the discrepancy lay in the determination of K_1. Consequently, the present investigation was restricted to a measurement of gas compositions in equilibrium with acids of various strengths.

Burdick and Freed passed nitrogen dioxide diluted with nitrogen through an absorption train containing nitric acid solution. The nitrogen oxides in the gas leaving were absorbed in alkali, the resulting solution analyzed for nitrate and nitrite, and the amounts of absorbed nitric oxide and nitrogen dioxide then calculated. The equilibrium was approached only from the nitrogen peroxide side. Abel, Schmid and Stein employed a static method wherein they measured the total pressure of the undiluted nitrous gases over a solution of nitric acid, and determined the partial pressure of nitrogen peroxide and tetroxide by comparing the spectrum of the equilibrium gas with that of a standard gas system. The present investigation also employed a static method but involved a chemical rather than spectrographic analysis of the equilibrium gas mixture. The measurements covered the range of acid strengths from 37 to 59% nitric acid, and temperatures from 15 to 35°. In this range the equilibrium partial pressures of nitric oxide and nitrogen peroxide are of the same order of magnitude and the analytical procedure employed is believed to be reliable. Data were obtained by approaching the equilibrium from both directions.

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(1) Burdick and Freed, THIS JOURNAL, **43**, 518 (1921).

(2) Taylor, *Ind. Eng. Chem.*, **17**, 633 (1925).

(3) Abel, Schmid and Stein, *Z. Elektrochem.*, **36**, 692 (1930).

(4) Abel, Redlich and Lengyel, *Z. physik. Chem.*, **132**, 189 (1928).

Experimental Procedure

The nitric acid used was C. P. grade (sp. gr. 1.42). This was diluted to the strengths used in the experiments with distilled water and analyzed by titration with standard alkali. Nitrogen dioxide was prepared by thermally decomposing lead nitrate. The nitrogen dioxide evolved was condensed and further purified by oxygen distillation. Nitric oxide was made by allowing sulfuric acid to react with sodium nitrite.[5] The nitrogen used as diluent was from cylinders and was of purity of 99.85% or better.

Figure 1 is a diagrammatic sketch of the reaction vessel and sampling apparatus. The reaction vessel (A) consisted of a 2-liter round-bottomed flask into which were sealed two capillary gas sampling tubes (B,B), a tap for measuring pressure (C), and a tube for introduction and removal of the liquid (D). The stopcocks on these taps were lubricated with vaseline, which withstood the actions of nitric acid and nitrogen dioxide very well. Air was removed by filling the flask with acid to be used in the experiment. About a liter of this acid was displaced with nitrogen and 400 to 500 cc. more with either nitric oxide or nitrogen dioxide. About 500 cc. of acid was left in the flask, this quantity being sufficient to ensure no appreciable change in the composition of the solution during the experiment. The reaction vessel was then immersed and shaken in a constant temperature bath controlled to ±0.02°. As a result of check runs it was found that equilibrium was attained within a period of four hours at all temperatures reported.

Samples were taken by means of the two modified Gaillard bulbs[6] (E,E). Prior to sampling, the first bulb containing 25 to 50 cc. of distilled water was evacuated and weighed. A measured amount of standard potassium permanganate solution made slightly acidic with sulfuric acid was added to the second. This bulb was evacuated and swept out with nitrogen several times to ensure complete removal of oxygen before weighing.

A mercury manometer (F) was connected to (C) to determine the pressure in the reaction vessel. The Gaillard bulbs were then connected to (B,B) and the tube from the bottle (H) to (D). Acid of the same strength as that in the reaction vessel was allowed to flow from (H) at such a rate that the samples would be obtained at constant pressure. The pressure was maintained constant by regulating cock (G). After sampling the Gaillard bulbs were again weighed, the increase in weight being a direct measure of the amount of sample obtained.

In the analysis of the gas phase, one is confronted with the problem of determining six constituents: water vapor, nitric acid vapor, nitric oxide, nitrogen dioxide, nitrogen tetroxide and nitrogen. Water was neglected, and the inert gas assumed to be only nitrogen. The error from this simplifying assumption affected the calculated value of K less than 1% in the worst case. From the analysis of the first bulb, the total nitrous oxides plus the nitric acid were determined. In this analysis the oxides were converted to nitric acid and determined as such. This method is a modification of that advanced by Gaillard[6] for determination of conversion efficiencies in the commercial oxidation of ammonia to nitric acid. The second or permanganate bulb gave a measure of the ratio of nitrogen dioxide plus tetroxide to nitric oxide. That permanganate will convert nitrous oxides to nitrate has been demonstrated by several investigators.[7] This procedure was checked experimentally by analyzing a mixture consisting of nitrogen and nitric oxide only. In accordance with theory, the equivalents of nitric acid per gram of sample formed in the first bulb were a third of the equivalents of permanganate per gram of sample reduced in the second.

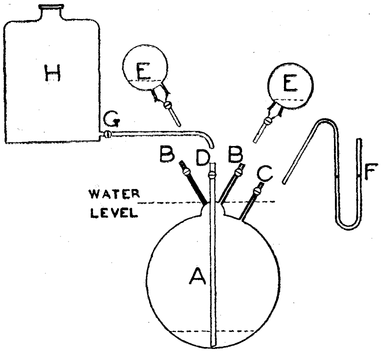

Fig. 1.

Oxygen was admitted to the first bulb with shaking until no further gas was taken up. This was taken as an indication that all the nitrous oxides had been converted to nitric acid. The solution in this bulb was then titrated with standard sodium hydroxide using methyl red as an indicator.

The bulb containing the permanganate was shaken for several hours to ensure completion of the reaction with nitric oxide. An excess of standard ferrous sulfate was added and the solution titrated to pink with permanganate. In this determination it was found that a large excess of potassium permanganate was necessary, as nitric oxide seemed to reduce it only as far as manganese oxide.

Taylor's data on the vapor pressure of nitric acid were used to calculate the amount of nitric acid taken in with the first sample, which value was applied as a correction to the titration of this sample. The ratio of dioxide to tetroxide was computed from Bodenstein's later values for the equilibrium constant.[8]

Results

The results are summarized in Table I and the calculated values of K_1 at 25° are plotted *vs.* acid strength in Fig. 2. In each case the pressures employed are in atmospheres and the logarithms are base 10. It is evident from the table that the results obtained starting with nitrogen peroxide check within the experimental error those obtained when starting with nitric oxide. Figure 2 also shows the results of Burdick and Freed and of Abel, Schmid and Stein. The vertical arrows indicate the extreme deviations of the results at a constant acid strength. It is evident that the

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(5) W. A. Noyes, THIS JOURNAL, **47**, 2170 (1925).

(6) Gaillard, *Ind. Eng. Chem.*, **11**, 745 (1919).

(7) Mellor, "Inorganic Chemistry," Longmans, Green and Co., New York, Vol. III.

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

TABLE I

SUMMARY OF RESULTS

Run	Temp., °C.	Nitric acid, %	Original gas	Equilibrium Pressures P_{NO_2}, atm.	Equilibrium Pressures P_{NO}, atm.	log K_1	log K_2	K	Mean K
37	15	54.5	NO	0.0348	0.0272	2.81	−4.59	0.017	0.019
38	15	54.5	NO_2	.0301	.0214	2.89	−4.59	.020	
35	20	54.7	NO	.0255	.0081	2.71	−4.40	.020	.018
36	20	54.5	NO_2	.0303	.0109	2.59	−4.40	.016	
15	25	37.2	NO_2	.0095	.0235	4.44	−6.20	.017	
17	25	37.1	NO_2	.0132	.0430	4.27	−6.20	.012	
18	25	37.1	NO	.0144	.0568	4.28	−6.20	.012	
30	25	40.7	NO_2	.0096	.0097	4.04	−5.80	.017	
31	25	40.7	NO	.0133	.0214	3.96	−5.80	.014	
32	25	40.7	NO_2	.0099	.0111	4.06	−5.80	.018	
19	25	48.5	NO_2	.0175	.0100	3.27	−4.91	.023	.017
20	25	48.4	NO	.0204	.0131	3.19	−4.91	.019	
21	25	48.4	NO_2	.0280	.0252	3.06	−4.91	.014	
22	25	58.8	NO	.0450	.0110	2.08	−3.74	.022	
23	25	58.8	NO	.0440	.0078	1.96	−3.74	.017	
24	25	58.8	NO_2	.0350	.0042	1.99	−3.74	.018	
39	30	54.6	NO	.0437	.0089	2.03	−4.03	.010	.011
40	30	54.5	NO_2	.0535	.0190	2.10	−4.03	.012	
33	35	54.8	NO	.0490	.0080	1.83	−3.86	.009	.010
34	35	54.7	NO	.0495	.0094	1.89	−3.86	.011	

present data support the results of Abel, Schmid and Stein rather than those of Burdick and Freed.

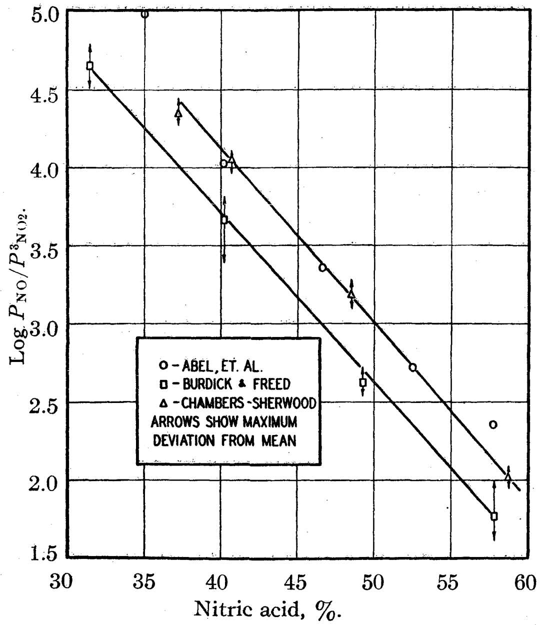

Fig. 2.

The mean value of K at 25° over the range of acid strengths studied is 0.017, which may be compared with 0.0046 from the results of Burdick and Freed and 0.019 obtained from the data of Abel, Schmid and Stein over the same range. The value of K reported by Abel, Schmid and Stein is 0.046, but this value was based only on two determinations at low acid strengths, where the partial pressures of nitrogen peroxide were very low.

It may be concluded that the results of Burdick and Freed are inaccurate, and that the data of Abel, Schmid and Stein, and those of the present investigation, serve as a more reliable basis for calculation of the equilibrium of this important reaction. It is difficult to suggest the source of error in the procedure used by Burdick and Freed, although it may be pointed out that they approached the equilibrium only from the peroxide side, and that failure to attain equilibrium would result in low values of K_1, as found.

It may be noted from Table I that K decreases with increased temperature, being 0.018 at 15° and 0.010 at 35°. The temperature range covered and the accuracy of the determinations are probably not great enough to justify a quantitative analysis of the trend of K with temperature, but it may be noted that the apparent temperature effect is considerably greater than that reported by Burdick and Freed, who found a 12% decrease in K on increasing the temperature from 25 to 75°.

Summary

The equilibrium of the reaction $3NO_2 + H_2O = 2HNO_3 + NO$ has been studied at 25° over the range of acid strengths from 37 to 59% nitric acid, and over the temperature range from 15 to

35° for an acid strength of 54–55% nitric acid. The results expressed in the form of the constant $K_1 = (P_{NO})/(P_{NO_2})^3$ agree well with the data of Abel, Schmid and Stein, deviating considerably from those of Burdick and Freed.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 17, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF NORTH CAROLINA]

The Infra-red Absorption of Heavy Acid Solutions

BY DUDLEY WILLIAMS AND E. K. PLYLER

A previous study[1] has revealed the presence of intense absorption bands at 2.4 μ and near 5.5 μ in the spectra of aqueous solutions of a number of acids. These bands were attributed to the effects of hydration. As the position of the band near 5.5 μ varied slightly with the solute, this absorption was identified with a characteristic frequency of an associational group containing undissociated acid molecules, while the 2.40 μ band was attributed to a hydrate in which the H^+ ion is involved. An investigation of the spectra of solutions of hydrolyzing salts gave additional support to this conclusion.[2]

The present work was undertaken in order to determine the changes in the positions of these bands caused by the substitution of deuterium for the hydrogen in the aqueous solutions. The deuterium oxide used as a solvent was a Norwegian product containing only a trace of ordinary water. The DCl solution was obtained from the California Isotope Company of Berkeley and contained about 0.5% H_2O. The D_2SO_4 and D_3PO_4 solutions were prepared by dissolving known amounts of the anhydrides in deuterium oxide. The sulfur trioxide used in this process was obtained by heating fuming sulfuric acid and the gas was allowed to pass through two drying tubes containing phosphorus pentoxide before entering the solvent. From specific gravity determinations it is estimated that the D_2SO_4 solution was approximately four normal and a D_3PO_4 solution of equal concentration was prepared. The spectroscopic methods have been described in a previous paper.[3] A rock-salt prism was used in the region from 2.5 to 12.0 μ, additional measurements being made in the 2.0–3.8 μ region with a fluorite prism. The absorbing layers used in the region of longer wave lengths were 0.02 mm. in thickness, while the layers in the 2.0–3.8 μ region were 0.05 mm. thick.

The infra-red absorption of deuterium oxide has been studied previously by Ellis and Sorge,[4] by Casselman,[5] and by the authors.[3] Intense bands have been observed at 2.85, 4.00, 6.80 and 8.20 μ. Although the broad band at 4.00 μ has three maxima, it was impossible to resolve this band into its components with the rock-salt prism used in the present work. The results obtained with deuterium oxide in the present study are given by the upper curve of Fig. 1. In addition to the bands shown in the figure, another band appeared at 10.4 μ. This band probably corresponds to the band recently observed at 8.6 μ in the spectrum of ordinary water.[6]

The transmission of the DCl solution is shown in the lower curves of Fig. 1. It will be noted that there is a marked increase in absorption near 5.5 μ. The dotted curve shows the transmission of a more concentrated solution of DCl in this region. There is also a slight increase in absorption near 3.4 μ, and this absorption may be seen more clearly when thicker absorbing layers are used. The results obtained in the 3 μ region with thicker cells are shown in another figure. With the exception of the increased absorption in the 3.4 and 5.5 μ regions of the solution spectrum, the transmission curve for the DCl solution bears a close resemblance to the D_2O curve. The curves are practically identical from 9 to 12 μ, and for this reason the transmission curves obtained in this region are omitted from the figure. The results obtained with the D_2SO_4 and D_3PO_4 solutions are the same as those obtained with the DCl except for the appearance of bands near 9 and 4.8 μ which are characteristic of the sulfate and phosphate

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[1] E. K. Plyler and E. S. Barr, *J. Chem. Phys.*, **2**, 306 (1934).

[2] E. K. Plyler and W. Gordy, *ibid.*, **2**, 470 (1934). Recent unpublished work, however, seems to indicate that the hydrated H^+ ion absorbs also in the region of 5.4 μ and the hydrated acid molecules absorb at slightly longer wave lengths.

[3] E. K. Plyler and D. Williams, *ibid.*, **4**, 157 (1936).

[4] J. W. Ellis and B. W. Sorge, *ibid.*, **2**, 559 (1934).

[5] A. L. Casselman, *Phys. Rev.*, **45**, 221 (1934).

[6] D. Williams, *ibid.*, **49**, 869 (1936).

groups. The spectra of compounds containing these groups have been studied extensively by reflection,[7] and regions of intense absorption appear at 9.0 μ in the sulfates and at 9.5 μ in the phosphates. These bands maintain their normal spectral positions even when the compounds are in solution.

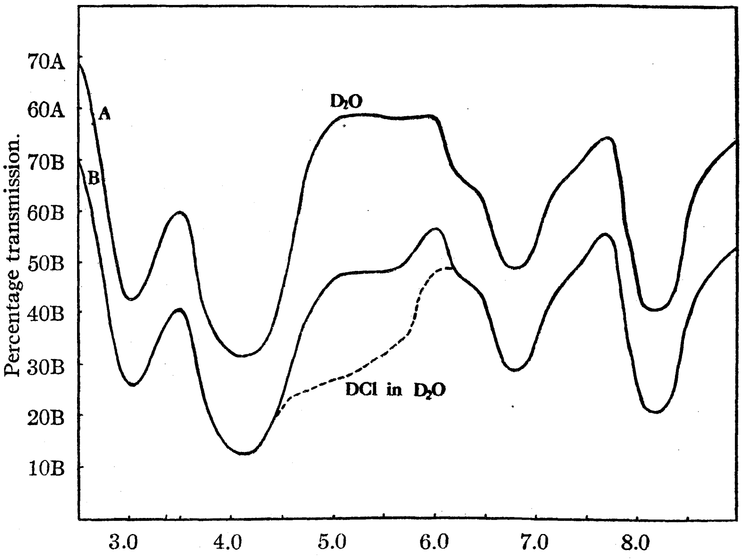

Fig. 1.—The percentage transmission of deuterium oxide and solutions of DCl: region, 2.5 to 9.0 μ.

In order to determine the positions of maximum absorption of the various solutions, curves were plotted showing the ratio of the solution transmission to the solvent transmission. The ratio curves for the 4.5–6.5 μ regions are shown in Fig. 2. As may be seen readily, all the solutions are strongly absorbing near 5.5 μ, the position of maximum absorption varying with the solution. The first two curves are plotted to the same scale and show the results obtained with two concentrations of DCl. It will be noted that increasing the DCl concentration causes additional absorption in the 4.9 μ region, where the absorption maximum of gaseous DCl appears, and it is possible that the absorption observed at this position may be caused by undissociated DCl molecules. However, the corresponding HCl band at 3.46 μ has never been observed in aqueous solution, and it would be surprising to find DCl molecules giving rise to a band of this type. The absorption of D_2SO_4 at 4.6 μ is the first harmonic of the SO_4 band at 9 μ mentioned above, and the D_3PO_4 band at 4.8 μ has a similar relation to the PO_4 maximum at 9.5 μ.

In Fig. 3 are given the results obtained between 2.0 μ and 3.8 μ with 0.05 mm. absorbing layers. The transmission determinations used in plotting the curves shown in this figure were made with a fluorite prism. The DCl curve given here was obtained with a sample of the less concentrated solution. The transmission curve shows intense absorption in the region of 3.4 μ. Increasing the concentration of DCl caused an increase in the intensity of this band, but a shift in position was not observed as in the case of the 5.5 μ region of absorption. The D_2SO_4 and D_3PO_4 solutions are also strongly absorbing in the 3.4 μ region, and additional absorption appears in the 2.2 μ region in the spectra of these latter solutions. The absorption in the 3.4 μ region is so intense that the plotting of ratio curves to aid in locat-

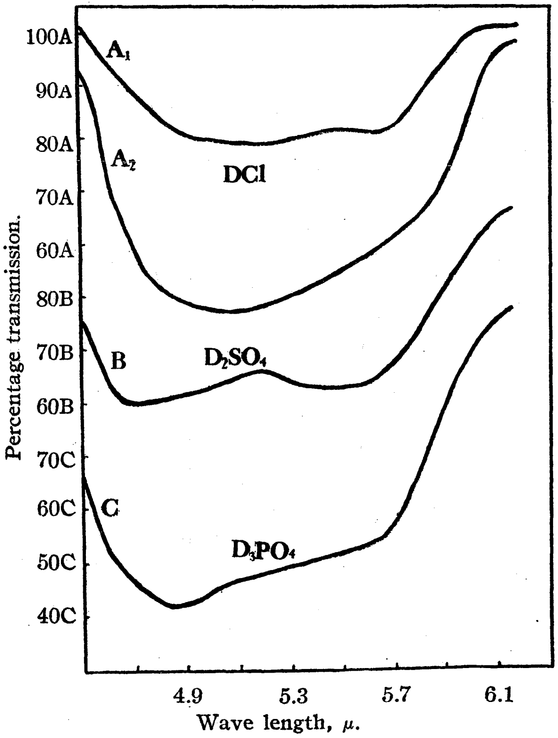

Fig. 2.—The ratio of the transmissions of acid solutions to deuterium oxide transmission: region, 4.5 to 5.8 μ; concentrations, DCl A_1, 3 *N*; DCl A_2, 5 *N*; D_2SO_4, 4 *N*; D_3PO_4, 4 *N*.

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[7] C. Schaefer and F. Matossi, "Das Ultrarote Spektrum," Verlag von Julius Springer, Berlin, 1930, p. 333.

ing the absorption bands is not deemed necessary.

It is interesting to note that the spectra of deuterium oxide solutions of the hydrolyzing salts potassium carbonate and sodium carbonate studied in a previous investigation[3] contain bands near 5.5 μ. Since similar bands appear in the spectra of the heavy acid solutions used in the present work, it is probable that the bands at 5.5 μ in the spectra of the salt solutions are caused by heavy carbonic acid formed on hydrolysis of the salts. In solutions of hydrolyzing salts of this type one would expect D_2CO_3 molecules to be much more numerous than D^+ ions, and hence it is possible that the 5.5 μ bands arise from the hydration of undissociated acid molecules. Other evidence in favor of this hypothesis lies in the slight variations in position of these bands in the different solutions, an effect to be expected if different negative radicals are present in the complex. The exact numbers and natures of the units entering into these associational groups cannot be determined from the data obtained in this study. It will be noted, however, that the position of the associational band produced by heavy acid molecules in deuterium oxide solutions is the same as that of the corresponding band produced by ordinary acids in aqueous solution. This seems to indicate that large groups are involved, since the replacement of hydrogen by deuterium does not produce an appreciable shift. Since the bands observed at 3.4 μ do not change their positions in the different acid solutions, it is probable that they are caused by the hydration of the D^+ ions. The corresponding bands in aqueous solutions of ordinary acids appear at 2.40 μ. Thus, the shift in the position of this absorption is what would be expected if the H in a simple R-H oscillator were replaced by deuterium to form R-D, where the mass of the accompanying group R is large as compared with H and D. The exact nature of the group R is at present unknown.

The experimental results obtained in this study indicate that the 2.4 μ band appearing in aqueous solutions of acids is shifted to 3.4 μ when the hydrogen is replaced by deuterium, while the bands in the 5.5 μ region are common to both types of solution.

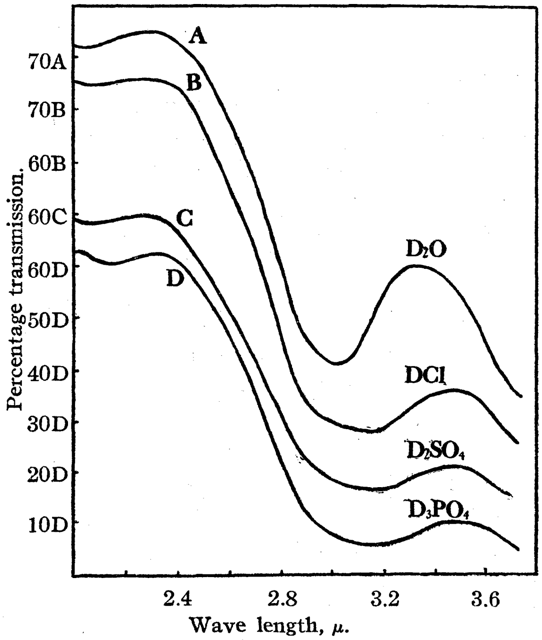

Fig. 3.—The transmission of deuterium oxide and three heavy acid solutions: region, 2.0 to 3.5 μ.

Abstract

The infra-red absorption of deuterium oxide and of DCl, D_2SO_4 and D_3PO_4 solutions has been measured in the region between 2 μ and 12 μ. In addition to the bands at 2.9, 4.0, 6.8 and 8.2 μ, a band at 10.4 μ has been found in the spectrum of deuterium oxide. In the spectra of all the heavy acid solutions studied intense absorption bands appear at 3.4 μ and near 5.5 μ in addition to the bands characteristic of the solvent. The solutions of D_2SO_4 and D_3PO_4 also give rise to characteristic SO_4 and PO_4 absorption, respectively. The intense bands at 3.4 and 5.5 μ are attributed to hydration effects.

GAINESVILLE, FLA. RECEIVED NOVEMBER 13, 1936

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

Conditions Affecting the Formation of Malonates and Barbiturates. Halogenalkyl Derivatives

BY GLENN S. SKINNER

In a previous paper[1] it was reported that better yields of a 5-β-hydroxyethyl-5-alkyl barbiturate are obtained by refluxing the reaction mixture for relatively short periods of time followed by the distillation of the alcohol. It has now been shown to be unnecessary to heat the reaction mixture according to the generally followed procedure of Fischer and von Mering. In fact, the observance of the more vigorous treatment causes a decrease in the yield. According to the procedure herein described yields of more than 90% are obtainable.

Experience also has been gained in the preparation of the necessary malonates. Using benzene as the medium it was found that ethylene bromide did not react with sodiophenylmalonic ester at temperatures below approximately 60°. This may explain why a previous attempt to carry out this condensation in ether was unsuccessful. While the reaction above this temperature is comparatively slow, it is possible to obtain yields of the corresponding lactone in excess of 50%.

In using an inert solvent as a medium it has been found possible to increase the yield of the *n*-butyl β-bromoethyl derivative from approximatively 52% (based on sodium) to 80% simply by using one equivalent of sodium to two of the other reactants. The finely divided sodium not only dissolves much more readily but the reaction with the halide takes place more rapidly. Trimethylene bromide has been reported to condense with sodioisoamylmalonic ester to give a 44% yield of the γ-bromopropyl derivative.[2] The yield may be increased to 68% by using the sodium, ester and bromide in the ratio 1:3:4. No solvent was used in this experiment and this yield could doubtless be further improved by a more extensive study. Here the reaction is more rapid and a very considerable amount of high boiling material is formed, hence the greater importance of having the bromide in excess of the other reagents. With ethylene bromide the amount of high boiling material is small and is only slightly increased by using the other reactants in excess of the sodium. The omission of a solvent and the use of a sodium:ester:bromide ratio as high as 1:6:2 instead of a 1:2:2 ratio in benzene shows no appreciable change in the yield of β-bromoethyl ester or high boiling residue based on sodium but a slight increase based upon the ester consumed in the process. Potassium is not as satisfactory as sodium since the potassium derivative shows a greater tendency to precipitate and the yields are lower. The reaction of both halides with ethyl phenylmalonate gives a sharp increase in the amount of high boiling material.

Before a recently described improvement[3] of the method for the preparation of phenylmalonic ester was published, we had made some study of the conditions during the preparation of a quantity of it for our work. It had been reported that ethyl carbonate[4] could be condensed with ethyl phenylacetate to give phenylmalonic ester in yields not greater than 20%. Accordingly the effect of potassium was studied with the result that 10% potassium–sodium alloy, 50% potassium–sodium alloy and potassium showed maximum yields of 45, 49 and 41%, respectively. The condensation of ethyl oxalate with ethyl phenylacetate by potassium is too vigorous to be controlled properly. With 10 and 50% alloys in benzene the yields of phenylmalonic ester were 77 and 71%, respectively, using a ratio of 1:2:1 for the metal, oxalate and phenylacetate. Under the same conditions using sodium the yield was 66%. Using ether as the medium and a 10% potassium–sodium alloy the comparative yield based on metal was 80 or 87% based on ethyl phenylacetate.

The tendency of ethyl phenylacetate to react with itself rather than ethyl carbonate is diminished by potassium judging from the amount of ethyl phenylacetate recovered and the weight of the high boiling residue. An increase of the carbonate/acetate ratio increases the yield of phenylmalonic ester and decreases the loss of ethyl phenylacetate. Increasing the acetate/metal ratio decreases the yield of phenylmalonic ester and increases the loss of ethyl phenylacetate.

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[1] Rosenberg, Kneeland and Skinner, THIS JOURNAL, **56**, 1339 (1934).

[2] Dox and Yoder, *ibid.*, **45**, 1757 (1923).

[3] "Organic Syntheses," **16**, 33 (1936).

[4] Nelson and Cretcher, THIS JOURNAL, **50**, 2759 (1928).

Markedly better results are obtained by the use of the metal, oxalate and phenylacetate in 1:2:1 ratio rather than the customary equivalent ratio.

5-β-Halogenethyl-5-alkyl barbiturates are formed in excellent yields by the action of the fuming halogen acids on the corresponding hydroxy compounds. The reaction proceeds smoothly for the bromides and iodides while the chlorides are formed with difficulty.

The γ-bromopropyl alkyl malonates are not converted to the lactones by distillation under similar conditions while, for example, β-bromoethyl phenylmalonate could not be distilled without decomposition to the lactone. This indicates a greater tendency for the formation of a five than a six-atom ring. Being an intramolecular temperature reaction this sharp difference is interesting especially as being in line with the older classical theory of ring formation. However, the experience that barbiturate formation takes place at ordinary temperatures encouraged the attempt to condense the halogen ester directly. The reaction mixture from γ-bromopropyl isoamylmalonic ester was successfully converted to γ-bromopropyl isoamylbarbiturate.

From the results of tests made through the courtesy of Dr. E. H. Volwiler of the Abbott Laboratories, β-iodoethyl and γ-bromopropyl isoamylbarbiturates appear to be the best tolerated and produce the most uniform depression. The latter employed intravenously in rabbits produced ataxia lasting one-half hour (300 mg./kg.) and Stage II anesthesia for one-half hour (500 mg./kg.).

Experimental Part

Halogenalkyl Malonates.—For the introduction of the β-bromoethyl group it is preferable to use the reagents in the following molal ratios: finely divided Na, 1.0; $RCH(CO_2C_2H_5)_2$, 2.0; $C_2H_4Br_2$, 2.0. The stirrer is run and the mixture is cooled during the addition of the alkylmalonic ester. If two mols of the ester is employed the complete solution of the sodium is fairly rapid. When the reaction slackens it is allowed to go to completion at room temperature. The ethylene bromide is added at once with stirring and cooling. The temperature of the bath is allowed to rise slowly to 70–75° where it is maintained for eight to ten hours. It is of no advantage to heat for longer periods to the disappearance of the last trace of alkali as the reaction is then substantially complete. The precipitation of sodium bromide begins near room temperature. However, if R is phenyl it is necessary to heat for seventy to seventy-five hours to secure substantial completion of the reaction, which does not begin until the temperature is near 60°. The phenyl bromoethyl compound could not be distilled without decomposition to the lactone which was obtained in only 52% yield.

Trimethylene bromide reacts more rapidly and the reaction flask must be surrounded with iced water at first. The mixture is then allowed to stand in a bath of water at room temperature for an hour and heated for about five hours at 70–75°. If R is phenyl the reaction begins near 45°. The phenyl derivative showed slight evidence of decomposition during distillation under diminished pressure with the bath at 220°, which is also indicated by the analysis. An attempt to convert the isoamyl derivative to the lactone by distilling it slowly at 196° (24 mm.) was unsuccessful.

n-Butyl γ-bromopropylmalonic ester: calcd. for $C_{14}H_{25}O_4Br$, Br 23.76%; found, Br 23.88%, b. p. 138 (2 mm.), n^{20}_D 1.4602; n^{25}_D 1.4580; d^{20}_4 1.188, d^{25}_4 1.182.

Phenyl γ-bromopropylmalonic ester: calcd. for $C_{16}H_{21}O_4Br$, Br 22.38%; found, Br 21.03%; b. p. 172° (1 mm.); n^{20}_D 1.5167, n^{25}_D 1.5143; d^{20}_4 1.274, d^{25}_4 1.269.

Ethyl Phenylmalonate.—From the results of ten runs in which both ether and benzene were used as solvents and the mass relationships were varied widely, the following procedure was selected as giving the best yield. Sodium (0.275 at.) and potassium (0.275 at.) are converted to a powdered alloy in the usual way except that overheating is avoided and the xylene is not removed. The alloy is covered with 250 cc. of dry benzene, cooled in finely crushed ice and at the incipient crystallization of the benzene a mixture of 0.50 mol. of ethyl phenylacetate and 2.00 mole of ethyl carbonate is added rapidly with mechanical stirring and readiness for additional cooling if necessary. The metal reacts completely within an hour. After standing for twenty-four hours and decomposing with a freezing mixture of ice and hydrochloric acid, there is obtained 1.20 mol. of ethyl carbonate, 0.116 mol of ethyl phenylacetate, 0.267 mol of ethyl phenylmalonate and 14 g. of residue. The malonate yield is thus 49% based on metal, 53% on ethyl phenylacetate used and 69% on ethyl phenylacetate consumed in the process. Similarly a 10% alloy gives a yield of 42% (metal) and a residue of 20 g. With 10% alloy, carbonate and phenylacetate in a 1:2:2 ratio the yield drops to 31% (metal) and the weight of the residue rises to 71 g. If the ratio is 1:4:2 the yield is 45% (metal) and the residue weighs 43.5 g. Pure potassium, carbonate and phenylacetate in a 1:2:1 ratio gives a yield of 41% (metal) and a residue of 20 g.

Similarly from an alloy of 0.055 at. potassium, 0.495 at. sodium, 250 cc. of dry ether, 1.00 mol of ethyl oxalate and 0.50 mol of ethyl phenylacetate there is obtained 0.418 mol of ethyl oxalate, 0.001 mol of ethyl phenylacetate, 0.437 mol of ethyl phenylmalonate and a residue of 10 g., corresponding to a yield of 80% (metal) and 87% (ethyl phenylacetate). With sodium alone under these conditions the yield dropped to 64 and 72%, respectively. Benzene, 50% alloy, and especially a lower oxalate–phenylacetate ratio decrease the yield.

Lactones.—The following new lactones are made by the distillation of the β-bromoethyl alkyl malonates under reduced pressure such that the material will not distil until the decomposition is complete. α-Carbethoxy-α-*n*-butyl-γ-butyric Lactone. Calcd. for $C_{11}H_{18}O_4$: C, 61.64; H, 8.47. Found: C, 61.1; H, 8.4; n^{20}_D 1.4487, n^{25}_D 1.4467;

d^{20}_4 1.063, d^{25}_4 1.059; b. p. 119 (3 mm.). α-Carbethoxy-α-phenyl-γ-butyric Lactone. Calcd. for $C_{13}H_{14}O_4$: C, 66.64; H, 6.03. Found: C, 66.6; H, 6.5, n^{20}_D 1.5211, n^{25}_D 1.5187; d^{20}_4 1.191, d^{25}_4 1.188; b. p. 145° (1 mm.).

β-Hydroxyethyl Barbiturates.—According to the following procedure the yield of β-hydroxyethyl-isoamylbarbituric acid has been increased from 75 to 89%. To a solution of sodium ethoxide prepared from 0.60 at. of sodium and 300 cc. of absolute alcohol is added 0.120 mol of lactone ester and then 0.40 mol of finely powdered urea. The flask is surrounded by a bath of water at room temperature and the stirrer is run until the urea dissolves. After standing until the next day a considerable amount of solid will have separated. A glassy residue remains after removal of the alcohol through a column under diminished pressure from a bath not heated above 50°. The aqueous solution is extracted with chloroform and the acid is precipitated with cooling by hydrochloric acid. An additional amount is obtained by extracting the filtrate with chloroform.

The yield of the *n*-butyl compound at the reflux temperature in six runs was 61–78% where the time of refluxing was one to five hours and the alcohol was distilled under diminished or ordinary pressure, the best yield being for a one-hour reflux. In one experiment where the alcohol was distilled at once and then under reduced pressure the yield was 75%. The yield was increased to 93% by mechanical stirring at a water-bath temperature of 45° to solution of the urea followed by distillation of the alcohol under reduced pressure. The acid melted at 147–148° which agrees with the value for the acid obtained by a different method.[5]

β-Halogenethyl Barbiturates.—β-Hydroxyethyl-isoamylbarbituric acid (0.20 mol) is heated with 200 cc. of fuming hydrobromic acid (55–60%) in 6 oz. (120 cc.) soda water bottles at a water-bath temperature of 55–60° for two hours with occasional shaking. The bottles are capped with crowns in which the cork has been replaced by disks of thin red gasket rubber. Bottles with wired well-ground glass stoppers also may be used. After standing at room temperature until the next day, 59 g. of crude product is obtained by suction filtration through sintered glass. One gram more is obtained by distillation of the filtrate under diminished pressure. The material is purified by dissolving in about three times its weight of warm alcohol, allowing to cool somewhat and stirring in an equal volume of ice water.

The preparation of the chlorides is more tedious, especially for the isoamyl derivative on account of its lesser solubility in the fuming acid. Here refluxing with four mols of thionyl chloride followed by the fuming acid treatment and repeated crystallization gives a pure product. The *n*-butyl derivative (0.050 mol) largely dissolves in 60 cc. of hydrochloric acid (1.19) at 60° with a current of hydrogen chloride passing through the mixture. The passage of the gas is continued while cooling in ice. After standing for two days at room temperature the material is filtered on sintered glass and washed with fuming acid. The crude material weighs 11.4 g. and melts at 138–139°. It must be crystallized repeatedly in the above manner in order to secure a sample melting sharply at 140°.

To prepare the iodide it is better to dissolve the hydroxy acid (0.19 mol) in 1.4 mol of ice-cold fuming 70% hydriodic acid. The solution is then allowed to stand for one day in a brown glass-stoppered bottle in the ice box, two days in a dark place at room temperature and finally one day in the ice box. The crude β-iodoethylisoamylbarbituric acid so obtained weighs 61 g. The filtrate heated to 50–60° for two hours and allowed to stand in the ice box gives 3 g. more. The material is crystallized from hot alcohol for the analysis. Two more crops melting at the same temperature (167°) are obtained by dilution, bringing the total yield of purified product to 58.5 g.

TABLE I

RR'C(CONH)$_2$CO

R	R'	M. p., °C.	Halogen, % Found	Halogen, % Calcd.	Yield, %
n-Butyl	β-Chloroethyl	140	14.28	14.38	92
n-Butyl	β-Bromoethyl	153.5	27.46	27.46	92
n-Butyl	β-Iodoethyl	192	37.53	37.55	92
Isoamyl	β-Chloroethyl	138.5	13.83	13.61	
Isoamyl	β-Bromoethyl	159.5	26.34	26.20	96
Isoamyl	β-Iodoethyl	167	36.18	36.05	91
Isoamyl	γ-Bromopropyl	150.5	24.73	25.05	40

γ-Bromopropyl-isoamylbarbituric Acid.—γ-Bromopropyl-isoamylmalonic ester (0.138 mol) when condensed with urea in the above manner gives 35.5 g. of a very viscous material which could not be induced to crystallize satisfactorily. This material when heated repeatedly with 100-cc. portions of 60% hydrobromic acid followed by the removal of the crystalline portion gives 25 g. of material melting at 143–147°. Repeated crystallization from chloroform did not give a pure product until after heating in an oven at its melting point (Table I). Further work is in progress.

Summary

1. The formation of 5-β-hydroxyethyl barbiturates is favored by lower temperatures than those heretofore employed for this reaction.

2. β-Bromoethyl and β-iodoethyl barbiturates are formed smoothly in excellent yields by the action of the fuming acids on the hydroxy compounds. The chloro compounds are also obtained but with more difficulty. γ-Bromopropyl-isoamylbarbituric acid was made although the desired intermediate lactone ester was not formed in the usual manner.

3. The use of two equivalents of malonate to one of sodium in making the desired halogenalkyl malonate is highly advantageous.

4. By the use of potassium and the adjustment of the mass relationships the yield of phenylmalonic ester is decidedly increased when either ethyl carbonate or ethyl oxalate is used.

NEWARK, DEL. RECEIVED SEPTEMBER 25, 1936

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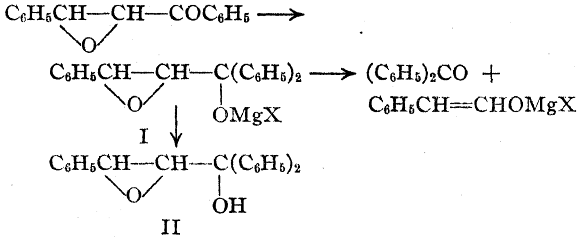
(5) Cretcher, Koch and Pittenger, THIS JOURNAL, **47**, 3084 (1925).

[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

The Action of Organometallic Compounds on Alpha Oxido Ketones

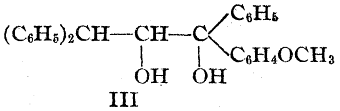
BY C. L. BICKEL

Alpha oxido ketones differing only slightly in structure behave quite differently when treated with phenylmagnesium bromide. Benzalacetophenone oxide reacts with one equivalent of phenylmagnesium bromide at −15°, giving the addition product I. Hydrolysis of this magnesium compound with acid gives the corresponding oxanol II. But at room temperature the magnesium compound I decomposes to give benzophenone and the magnesium derivative of the enolic form of phenyl acetaldehyde, a reaction represented below.

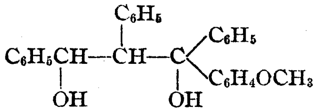


The oxide ring is not opened by phenylmagnesium bromide except through cleavage.[1] *o*-Chlorobenzalacetophenone oxide behaves in an analogous manner, opening of the oxide ring taking place only by cleavage of the magnesium derivative of the carbinol at higher temperatures.[2] Both of the above oxido compounds give a similar reaction with lithium phenyl, except that the lithium derivative of the carbinol decomposes more slowly.[2]

Conversely, Bergmann[3] found that benzal-*p*-methoxyacetophenone oxide behaves quite differently with phenylmagnesium bromide. His results indicated that two equivalents of reagent add to the oxide at room temperature with no resultant cleavage. Bergmann did not determine the structure of this product, but offered two possible structures, III and IV.



III

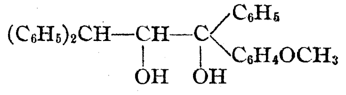


IV

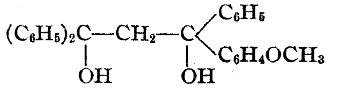
Either of these compounds would be formed by fission of the oxide ring and attendant addition. The point at which the ring opens would determine the nature of the product.

The present paper is concerned with the reaction of benzal-*p*-methoxyacetophenone oxide with lithium phenyl, a more detailed study of the reaction with phenylmagnesium bromide and the determination of the structure of the product first obtained by Bergmann.

Chromic acid oxidation of the compound obtained by Bergmann gave benzophenone and *p*-methoxybenzophenone as products. Only two compounds, III and VI, which could have been formed in the Grignard reaction would give these two oxidation products.



III



VI

Compound VI would be formed by rearrangement of the oxide to give a ketone which would add phenylmagnesium bromide. Compound III would be formed by the opening of the oxide ring by phenylmagnesium bromide with attendant addition.

The tertiary carbinol VI was synthesized from the beta diketone VII, the first reaction with phenylmagnesium bromide giving the two isomeric compounds VIIA and VIIB. The treatment of each of these isomers with lithium phenyl gave the carbinol VI, whose structure was confirmed by oxidation to benzophenone and *p*-methoxybenzophenone. The synthesis is represented by the accompanying formulas.

The carbinol VI was not identical with the product obtained from the *p*-methoxy oxide. Therefore, by elimination, the structure of the product obtained by Bergmann is represented by formula III.

A most interesting result was obtained when benzal-*p*-methoxyacetophenone oxide was treated with lithium phenyl in ether solution. None of

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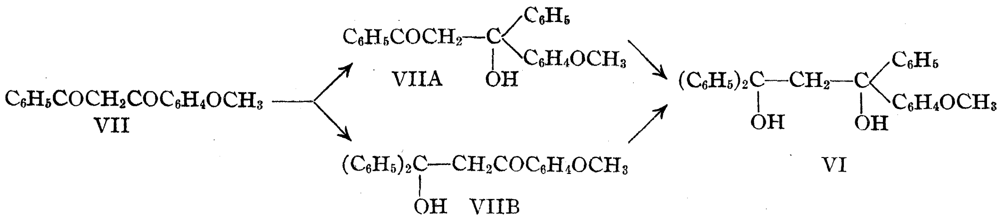
(1) Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 205 (1931).

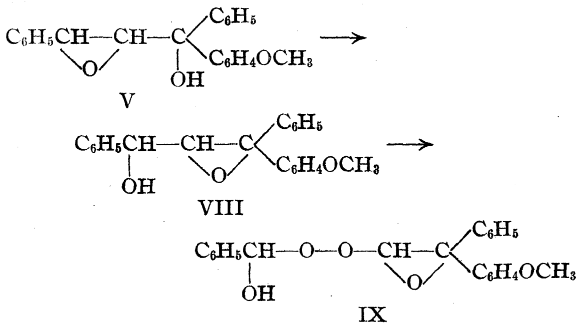
(2) Kohler and Bickel, *ibid.*, **57**, 1099 (1935).

(3) Bergmann and Wolff, *ibid.*, **54**, 1644 (1932).



the compound III could be obtained. Instead, the oxide gave results analogous to those obtained with benzalacetophenone oxide or the corresponding *o*-chloro compound. In cold solution the oxanol V was the only product; at room temperature the expected cleavage of the oxanol V took place. The glycol III was produced in good yield when the oxanol V was treated with excess phenylmagnesium bromide.

The oxanol V behaves like the corresponding unsubstituted oxanol II when treated with a dilute alcoholic solution of sodium hydroxide. An isomeric oxanol VIII is produced. This oxanol is apparently much more unstable than the other known compounds of similar structure, cleavage and autoxidation proceeding very rapidly in the laboratory air. Indeed it is difficult to obtain a pure sample and it is more difficult to keep a pure sample long enough to determine its percentage composition, crystal form and melting point with any great degree of accuracy. Cleavage and autoxidation of this oxanol give a peroxide IX which forms benzoic acid and *p*-methoxybenzophenone by chromic acid oxidation.



Bergmann treated the oxide with excess of phenylmagnesium bromide at room temperature. One equivalent of phenylmagnesium bromide added inversely to a cold solution of the oxide should provide the best conditions for the production of the oxanol V. Yet when these conditions were fulfilled, 50% of the oxide was recovered unchanged and the remaining 50% was converted into the product obtained by Bergmann.

The inactivity of the oxide ring of the *p*-methoxy compound toward lithium phenyl suggests the possibility that oxide rings in general are unattacked by lithium phenyl under conditions which would give a reaction with phenylmagnesium bromide. Experiments now in progress will attempt to settle this question.

An explanation of the difference in the reaction of benzalacetophenone oxide and benzal-*p*-methoxyacetophenone oxide with phenylmagnesium bromide is as yet not evident. At least two explanations can be offered from the facts at hand. The anisyl group may activate the oxide ring so that fission of the oxide ring is made much easier. This would permit simultaneous addition to the carbonyl group and to the oxide ring, producing a magnesium derivative having no tendency to break up. The alternative is that the anisyl group strengthens the C–C bond between the carbonyl group and the oxide ring, thus preventing the cleavage of the primary magnesium derivative.

The fact that the anisyl compound shows addition to the oxide ring at low temperatures—while the unsubstituted oxide does not—indicates that the first explanation is more probably correct. Research now in progress may provide a more adequate explanation for this difference in behavior.

Experimental Part

2-Hydroxy-1,3,3-triphenyl-1-anisyl Propanol, III

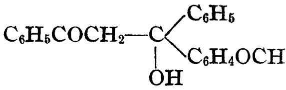
Inverse Grignard.—One equivalent of phenylmagnesium bromide in ether was added slowly to a stirred solution of 15 g. of benzal-*p*-methoxyacetophenone oxide in 300 cc. of ether maintained at −15°. The cold solution was stirred for thirty minutes after complete addition of the reagent and was then decomposed immediately with iced acid. The ether yielded 12 g. of the 132° compound III described by Bergmann, in addition to 4 g. of unchanged oxide. About 3.5 g. of unchanged oxide was also reclaimed from the solid clinging to the walls of the reaction flask.

Excess Grignard.—To a stirred solution of four equivalents of phenylmagnesium bromide in ether was added 15 g. of solid benzal-*p*-methoxyacetophenone oxide. After boiling the stirred solution for one hour the product was isolated in the usual way. The yield was 23.5 g. of the 132° compound III, compared with a calculated yield of 24.2 g.

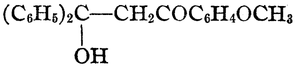
Oxidation.—Chromic acid oxidation of the carbinol III in glacial acetic acid solution gave benzophenone and *p*-methoxybenzophenone, identified by means of known samples. No benzoic acid could be detected.

3-Hydroxy-1,3,3-triphenyl-1-anisyl Propanol, VI.—To a stirred solution of four equivalents of phenylmagnesium bromide in ether was added in the course of two hours 25 g. of *p*-methoxydibenzoylmethane suspended in ether. After the mixture had been stirred and refluxed for four hours, hydrolysis with iced acid was accomplished as usual. The product was fractionally crystallized from methyl alcohol (kept slightly acid with glacial acetic acid to prevent cleavage), giving about 7 g. each of two isomeric compounds.

The 132° isomer VIIA is much more insoluble in methyl alcohol and crystallizes in small needles. Oxidation by chromic acid in glacial acetic acid solution gave benzoic acid and *p*-methoxybenzophenone. The 132° isomer is therefore



The 118° isomer VIIB is quite soluble in methyl alcohol and crystallizes in small needles. Oxidation by chromic acid gave anisic acid and benzophenone. The 118° isomer is therefore



$$(C_6H_5)_2\underset{\displaystyle OH}{\underset{|}{C}}—CH_2COC_6H_4OCH_3$$

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.48; H, 6.07. Found: (132°) C, 79.36; H, 6.17; (118°) C, 79.31; H, 6.20.

Lithium Phenyl and the (118°, 132°) Isomer.—To a stirred solution of four equivalents of lithium phenyl in ether cooled to 0° was added 3 g. of the 132° isomer suspended in a small volume of ether. After two hours of stirring at 0° the solution was hydrolyzed in the usual way with iced acid. The dried ethereal solution, diluted with petroleum ether, deposited clusters of stout needles melting at 150°. The yield was about 3 g. The carbinol is fairly soluble in ether, quite soluble in methyl alcohol and insoluble in petroleum ether. The 118° isomer gave the same 150° carbinol in a similar reaction.

Anal. Calcd. for $C_{28}H_{26}O_3$: C, 81.91; H, 6.39. Found: C, 81.86; H, 6.37.

Oxidation.—Chromic acid oxidation of the carbinol VI gave benzophenone and *p*-methoxybenzophenone, identified by means of known samples.

2-Oxido-1,3-diphenyl-1-anisyl Propanol, V.—To a stirred solution of one equivalent of lithium phenyl in 200 cc. of ether maintained at −15° was added 10 g. of solid benzal-*p*-methoxyacetophenone oxide over a period of thirty minutes. Forty-five minutes of additional stirring at −15° produced a precipitate. Decomposition of this reaction mixture with iced acid gave an ether solution which deposited large plates melting at 136°. The yield was 12 g. None of the carbinol III could be detected. The oxanol V is quite soluble in acetone, moderately soluble in ether, insoluble in petroleum ether and forms beautiful plates from an acetone–petroleum ether mixture.

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.48; H, 6.07. Found: C, 79.36; H, 6.12.

Oxidation.—Chromic acid oxidation of the oxanol V gave benzoic acid and *p*-methoxybenzophenone, identified by means of known samples.

Addition of Phenylmagnesium Bromide.—Two grams of solid V was added to a stirred solution of three equivalents of phenylmagnesium bromide in ether. After being boiled for one and one-half hours the solution was treated with iced acid and the product isolated in the usual way. The ether gave 2.5 g. of the 132° compound III, identified by a mixed melting point with known material.

Cleavage with Lithium Phenyl.—A stirred ether solution of three equivalents of lithium phenyl to which 5 g. of the solid V had been added was boiled for three hours. After decomposition with iced acid, the only solid product which could be isolated was *p*-methoxytriphenylcarbinol, identified by means of a known sample. The remaining material was the usual resinous aldehyde.

Rearrangement with Bases: 2-Oxido-1,3-diphenyl-3-anisyl Propanol, VIII.—To a solution of 0.2 g. of potassium hydroxide in 100 cc. of methyl alcohol was added 5 g. of the sparingly soluble oxanol V. The mixture was allowed to stand for three days during which time the solid gradually dissolved, then poured into ice water. The product crystallized from ether–petroleum ether in stout plates melting at about 120°. The melting point of the pure substance was not determined exactly because of very rapid deterioration in laboratory air. The rearrangement product is very soluble in methyl alcohol, acetone and ether and is but sparingly soluble in petroleum ether. No other product was isolated except the peroxide formed by autoxidation of VIII. The rapid decomposition of the compound made an accurate analysis most difficult.

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.48; H, 6.07. Found: C, 79.1; H, 5.9.

Oxidation.—Chromic acid oxidation of the oxanol VIII gave only benzoic acid and *p*-methoxybenzophenone as products.

Autoxidation: The Peroxide, IX.—The oxanol VIII is autoxidized very rapidly in the air of the laboratory. A freshly prepared sample oiled and developed the odor of benzaldehyde after a few minutes of exposure. Complete autoxidation gave a white powder which was recrystallized from ether–petroleum ether. It separates as fine white needles and melts with brisk bubbling at 150°. It is sparingly soluble in acetone, methyl alcohol and ether and insoluble in petroleum ether.

Anal. Calcd. for $C_{22}H_{20}O_5$: C, 72.48; H, 5.54. Found: C, 72.4; H, 5.7.

Oxidation.—Chromic acid oxidation of the peroxide IX gave benzoic acid and *p*-methoxybenzophenone as products.

2-Oxido-1,1,3-triphenyl Propanol.[4]—Ten grams of solid benzalacetophenone oxide was added to a stirred solution of two equivalents of lithium phenyl in ether maintained at −15°. After forty-five minutes of stirring at −15° the solution was decomposed with iced acid. The ether gave a good yield of the 130° oxanol previously obtained by the use of phenylmagnesium bromide. The identity of the compound was verified by a mixed melting point with known material.

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[4] Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 214 (1931).

2-Oxido-1,1-diphenyl-3-(*o*-chlorophenyl) Propanol.[5]—Ten grams of solid *o*-chlorobenzalacetophenone oxide was added to a stirred ethereal solution of two equivalents of lithium phenyl maintained at −15°. After forty-five minutes of stirring at −15°, the solution was decomposed with iced acid. The ether gave a good yield of the 107–108° oxanol previously obtained by the use of phenylmagnesium bromide. The oxanol was identified by comparison with a known sample.

The author gratefully acknowledges a gift from the Milton Fund of Harvard University, with which the starting materials used in this problem were purchased.

Summary

The action of lithium phenyl and of phenylmagnesium bromide on alpha oxido ketones is compared. The structure of the compound formed by the reaction of phenylmagnesium bromide and benzal-*p*-methoxyacetophenone oxide has been determined.

EXETER, N. H. RECEIVED DECEMBER 16, 1936

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[5] Kohler and Bickel, THIS JOURNAL, **57**, 1100 (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND MILLS COLLEGE]

Stereochemistry of Deuterium Compounds. I. Optical Rotation of Methylhexyldeuterocarbinol

BY LEONA YOUNG AND C. W. PORTER

Many unsuccessful attempts have been made to obtain optically active compounds in which asymmetry is dependent upon differences between hydrogen and deuterium. It was our aim, a year ago, to prepare stereoisomeric compounds of the type RR'CHD and to isolate the *d* and *l* forms of these compounds. Attempts to prepare such compounds from optically active halides, through the Grignard reaction, led to complete racemization.[1] Attempts to isolate an optically active hydrocinnamic acid from the products formed when cinnamic acid was reduced by deuterium failed, presumably, on account of slight differences in the solubilities of the alkaloid salts. Failure to resolve racemic phenyldeuteroacetic acid, C_6H_5-CHD-COOH, into active components through fractional crystallization of alkaloid salts was attributed to the same cause.[2]

Biilman, Jensen and Knuth claim to have produced a measurable optical rotation in camphane through the substitution of deuterium for hydrogen in a methylene group[3] but their findings have not been confirmed and their technique has been the subject of adverse criticism.[4]

Recently we turned our attention to a comparison of the rotations of compounds in which the hydrogen and deuterium are not attached directly to the asymmetric carbon atom. One example of this type has been reported.[5] Methyl hexylcarbinol was resolved into active components and the dextrorotatory fraction was used in the experiments reported here. The active alcohol was esterified by treatment with acetyl chloride and the ester was, in turn, hydrolyzed with deuterium oxide. The rotation of the recovered alcohol was lower than that of the original sample. This alcohol was then reconverted into the original form through esterification and subsequent hydrolysis with ordinary water. The recovered compound had the same rotation as that of the original sample. The experiment was repeated several times and, within the limits of experimental error, the results were the same.

The measured rotations were as follows:[6]

	I	II	III
Original carbinol	17.45	19.00	17.90
Deuterium derivative	17.20	18.70	17.60

The average difference in rotations of the two compounds was 0.28 scale divisions or 0.11°. We feel justified, therefore, in reporting a real difference between the optical properties of ordinary methylphenylcarbinol and the compound formed

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[1] Porter, THIS JOURNAL, **57**, 1436 (1935).

[2] Schultz and Porter, unpublished work, 1935.

[3] Biilman, Jensen and Knuth, *Ber.*, **69**, 1031 (1936).

[4] Leffler and Adams, THIS JOURNAL, **58**, 1555 (1936).

[5] Clemo and McQuillen, *J. Chem. Soc.*, 808 (1936).

[6] The measurements were made with a Fric polarimeter. The scale divisions on this instrument are equivalent to 0.404 degrees. The reading +19.00 corresponds to 7.68°. The specific rotation of the pure dextro compound with green light (5461 Å.) is +11.80°. Our resolution of the racemic mixture was not quantitative but for the purpose of this study it was not necessary to have complete separation. It was necessary only to have a preparation of known rotatory power and to be sure that no racemization occurred in the treatment to which the compound was subjected.

by substituting deuterium for hydrogen in the hydroxyl group. The specific rotation of the deuterium compound, $[\alpha]^{17}_{5461}$, is +11.62°.[7]

In earlier attempts to replace the carbonyl hydrogen by deuterium the alcohol was converted into the sodium derivative and the sodium alcoholate was hydrolyzed by deuterium oxide. This treatment caused partial racemization. On the other hand, acetyl chloride acts upon the optically active alcohol without racemization and the acetyl derivative when hydrolyzed by dilute sodium hydroxide or by a solution of sodium ethylate yields the original alcohol without change in rotation.

The acetyl derivative of 2-octanol is very slightly soluble in water and the hydrolysis is necessarily accomplished in alcoholic solution. To guard against an exchange between the hydrogen of the hydroxyl group in the ethyl alcohol (used as a solvent) and deuterium in the hydroxyl group of the octyl alcohol, we hydrolyzed the ester in a mixture of NaOD, C_2H_5OD and D_2O when the heavy derivative was wanted and we used a mixture of NaOH, C_2H_5OH and H_2O when the light alcohol was wanted.

Experimental

The Resolution of Methylhexylcarbinol.—The standard method for the resolution of a racemic mixture of methylhexylcarbinol into its optical isomers was employed.[8]

Preparation of the Acetyl Derivative.—Thoroughly dried dextrorotatory methylhexylcarbinol was converted into the acetyl derivative by means of acetyl chloride. Slightly more than the equivalent weight of acetyl chloride was added to the alcohol, drop by drop and with constant stirring, at a temperature of from 10 to 15°. The mixture was allowed to stand overnight at room temperature. The excess of acetyl chloride was then distilled off on a water-bath. The remaining acetyl derivative of the alcohol was obtained by distillation under reduced pressure.

Preparation of the Deuterium Derivative.—One half of the acetyl derivative of the dextrorotatory methylhexylcarbinol (17.68 g.) was dissolved in 120 cc. of C_2H_5OD and 40 cc. of D_2O. To this was added 10 g. of NaOD. The solution was heated for one hour under a reflux condenser on a water-bath. The ethyl alcohol was then distilled off by immersing the flask in boiling water. When nearly all the ethyl alcohol had been removed the remaining mixture separated into two layers. The upper layer (methylhexylcarbinol) was removed and dried with anhydrous potassium carbonate. It was then fractionated to remove traces of ethyl alcohol and treated again with potassium carbonate. The process of alternate distillation and treatment with potassium carbonate was continued until there was no further change in rotatory power, *i. e.*, until all water and ethyl alcohol had been removed. The rotation was lower than that of the original alcohol as indicated in the table above.

The remaining half of the acetyl derivative of the methylhexylcarbinol was treated in the same way with NaOH, C_2H_5OH and H_2O. The final product showed no difference in optical rotation from that of the original substance. The result indicates that this method of esterification and hydrolysis does not cause racemization of the alcohol.

Conversion of the Deuterium Derivative of Methylhexylcarbinol to the Hydrogen Derivative.—The deuterium derivative of methylhexylcarbinol was converted into the acetyl derivative as described above. The ester was hydrolyzed in a solution of NaOH, C_2H_5OH and H_2O. The product was dried and distilled as previously described and its rotation returned to the original value.

Summary

Substitution of deuterium for hydrogen in the hydroxyl group of methylhexylcarbinol lowers the optical rotation of the compound.

BERKELEY, CALIF.

RECEIVED NOVEMBER 23, 1936

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(7) Calculated from the measured rotation and known composition of the sample used. The specific rotation of ordinary 2-octanol is 11.80°. Our mixture consisting of *d*- and *l*-octanol had a rotation of +7.68°. This value is equal to $11.80\ M_1 - 11.80 M_2$ with M_1 and M_2 representing the mole fractions of the dextro and levo rotatory forms, respectively. The mole fraction of the *d*-form in the mixture is, therefore, 0.825 and of the *l*-form 0.175. The mole fractions are the same after conversion to the deuterium derivatives and this mixture in a 10-cm. tube has a rotation of 7.55°. From the equation $7.55 = 0.825\alpha - 0.175\alpha$ we obtain $\alpha = 11.62°$.

(8) "Organic Syntheses," Vol. VI, 1926, p. 68.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

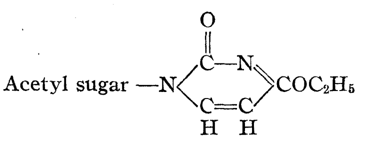
Synthetic Nucleosides—Some 1-Glycosidouracils

BY GUIDO E. HILBERT

Of the two known methods for synthesizing pyrimidine nucleosides, the one most recently introduced,[1] involving the interaction of 2,4-dialkoxypyrimidines and acetobromosugars, has the distinct advantage of actually introducing the sugar into the pyrimidine ring at the 1-position, which is that occupied by ribose in uridine and cytidine. Unfortunately the method seemed not to be as general as first expected. For example, two other types of pyrimidines, namely, 2-methoxy-4-amino-[2] and 2,4-dimethoxy-5-methyl-pyrimidine[3] formed in the presence of acetobromoglucose only methylated derivatives. These results suggest that the success of the method is dependent to a marked extent upon the nature of the substituents attached to the pyrimidine cycle. The following investigation was initiated (a) to test the generality of the reaction between various acetobromosugars and 2,4-diethoxypyrimidine and (b) with the hope of obtaining compounds similar in constitution to the anomalous 4-ethoxy-2-triacetyl-*d*-ribosidopyrimidine (I) obtained as a by-product in the interaction of acetobromo-*d*-ribose and 2,4-diethoxypyrimidine.[4] If such a product could be formed from an easily accessible sugar, there would be no difficulty in the way of obtaining sufficient material for a proof of structure.

Four different sugar derivatives, namely, acetobromo-*d*-galactose, acetobromo-*d*-xylose, acetobromo-*l*-arabinose and acetobromo-*d*-mannose, were used in this work. Each of the first three gave with 2,4-diethoxypyrimidine compounds of the type (II); in none of these reactions could crystalline analogs of the labile 4-ethoxy-2-triacetyl-*d*-ribosidopyrimidine (I)[4] be isolated. Considering the number of side reactions that are possible (see below), the yields of the 1,2-dihydro-2-keto-4-ethoxy-1-acetylglycosidopyrimidines (II) are quite satisfactory. The products (II) were converted by simultaneous deacetylation and deëthylation with alcoholic hydrogen chloride into the corresponding 1-glycosodouracils, which, like uridine, neither respond to the Wheeler-Johnson color test nor reduce Fehling's solution after acid treatment. It is interesting that the pentose-pyranosidouracils melt considerably higher, are thermally more stable and are much less soluble in water than uridine and the hexose–pyranosidouracils. Evidently the presence of a carbinol side group on a sugar ring affects significantly the properties of the nucleosides.

(II)



Of the acetobromosugars investigated, acetobromo-*d*-mannose, because of the similarity of its chemical reactions with those of acetobromo-*d*-ribose ("orthoacetate" formation[5]), was considered to offer the most promise of producing an analog of (I). Unfortunately, the interaction of acetobromo-*d*-mannose and 2,4-diethoxypyrimidine gave a sirup and the lability of the desired product precluded fractionation of the sirup to remove by-products. In view of the sluggishness with which most mannose derivatives crystallize and the complexity of the reaction product, this result was not altogether unexpected. However, presumptive evidence in favor of the formation of an analog of (I) in this reaction was obtained in the following manner. When the sirup was allowed to stand for a considerable length of time, a crystalline material gradually deposited. After separation and purification it proved to be 1,2-dihydro-2-keto-4-ethoxypyrimidine,[6] which had been obtained previously from the mild alkaline hydrolysis of (I). Presumably this was formed by the slow hydrolysis of 4-ethoxy-2-tetraacetyl-*d*-mannosidopyrimidine. Since the formation of a pyrimidine substituted in the 1-position by mannose was of less immediate interest, no effort was made to prepare 1-*d*-mannosidouracil by using a procedure similar to that employed for the isolation of 1-*d*-ribosidouracil.[4]

The 1,2-dihydro-2-keto-4-ethoxy-1-acetylglycosidopyrimidines (II) represented only a minor fraction of the product formed by the interaction

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[1] Hilbert and Johnson, THIS JOURNAL, **52**, 4489 (1930).

[2] Hilbert, *ibid.*, **56**, 190 (1934).

[3] Schmidt-Nickels and Johnson, *ibid.*, **52**, 4511 (1930).

[4] Hilbert and Rist, *J. Biol. Chem.*, in press.

[5] Levene and Tipson, *ibid.*, **92**, 109 (1931).

[6] This was also a secondary product of the interaction between acetobromo-*d*-galactose and 2,4-diethoxypyrimidine.

of 2,4-diethoxypyrimidine and acetobromosugars. Considerable ethyl bromide was formed, presumably by the degradation of the intermediate pyrimidinium bromide, and interacted competitively with 2,4-diethoxypyrimidine to give 1,2-dihydro-2-keto-1-ethyl-4-ethoxypyrimidine. This was separated readily from the other products of the reaction and on treatment with hydrogen chloride gave 1-ethyluracil quantitatively. A previous attempt to carry out the graded ethylation of 2,4-diethoxypyrimidine with ethyl iodide[7] was unsuccessful and gave only the end-product, 1,3-diethyluracil. In a few reactions, the by-products, 1,2-dihydro-2-keto-4-ethoxypyrimidine, mentioned above, and uracil, in traces, were also formed. Little is known regarding the other and major side product or products. In one instance, a mixture resulting from the interaction of acetobromo-*d*-glucose with 2,4-diethoxypyrimidine was fractionated and the material that did not crystallize distilled in a high vacuum (0.0001 mm.). Analysis of the distillate which could not be made to crystallize indicates that it is a tetraacetylglucosidoethoxypyrimidine.

From the preceding results and those previously published on 2,4-diethoxypyrimidine, it may be concluded that, although the reaction with acetobromoglycosides is quite complex, a certain amount of the sugar will enter the 1-position of this particular type of pyrimidine. This is of interest because, of the various pyrimidines that could be studied in the above type of reaction, the 2,4-diethoxy derivative is probably the most important, since its use can be directed not only to the preparation of analogs of uridine but also indirectly to those of cytidine.[8] As the synthesis of this type of compound seems to be independent of the kind of acetobromoglycoside used, it is believed that the synthesis of the naturally occurring pyrimidine nucleosides now resolves itself primarily into a sugar problem.

I wish to express my appreciation to Dr. R. T. Milner and Mrs. M. S. Sherman for performing the microanalyses recorded.

Experimental

Acetobromo-*d*-xylose,[9] acetobromo-*d*-mannose and acetobromo-*d*-galactose were prepared from the acetates by the method of Levene and Raymond.[10] Acetobromo-*l*-arabinose[11] was prepared directly from *l*-arabinose according to Hudson's[12] modification of the method of Chavanne.[13] All the acetobromoglycosides used in this work were recrystallized several times, generally from dry ether–petroleum ether. Acetobromo-*d*-galactose, which has rarely been obtained crystalline, melted at 87–88°[14,15]; $[\alpha]^{21}_{D}$ +216° (c = 7.44 in U. S. P. chloroform).

The reaction between 2,4-diethoxypyrimidine and the acetobromoglycosides was carried out in an oven (temperature control). Since considerable ethyl bromide is evolved in the reaction it is desirable to connect the flask containing the reactants with a glass tube leading to the outside atmosphere; the portion projecting from the furnace was fitted with a tube containing a drying agent.

1,2-Dihydro-2-keto-4-ethoxy-1-triacetyl-*d*-xylosidopyrimidine.—A mixture of acetobromo-*d*-xylose (38 g.) and 2,4-diethoxypyrimidine (38 g.) was heated at 65° for eighteen hours. After thirty minutes there was complete solution and in two hours large colorless plates started to separate. The final reaction mixture consisted of a mush of crystals in a pale yellow sirup. It was treated with 15 cc. of dry ether, filtered and the solid washed with ether; yield, 14 g. (31% of the theoretical yield based on the acetobromo-*d*-xylose or 16% based on 2,4-diethoxypyrimidine). The product was recrystallized from 150 cc. of 95% ethyl alcohol and deposited as needles on rapid cooling; m. p. 218° resolidifying at 200°; $[\alpha]^{22}_{D}$ 58.4° (c = 5.14 in U. S. P. chloroform). This xyloside was very soluble in cold chloroform, soluble in hot alcohol, slightly soluble in ether and sparingly soluble in water.

Anal. Calcd. for $C_{17}H_{22}O_9N_2$: C, 51.23; H, 5.57; N, 7.04; OC_2H_5, 11.31. Found: C, 51.35; H, 5.51; N, 6.96; OC_2H_5, 11.24.

The original sirup from which the nucleoside had been filtered, after standing for several hours, deposited an additional small quantity of the nucleoside, which was contaminated with a finely divided material. The latter was separated mechanically; it did not melt at 300° and was probably uracil.

1,2-Dihydro-2-keto-4-ethoxy-1-*d*-xylosidopyrimidine.—A solution of 3 g. of 1,2-dihydro-2-keto-4-ethoxy-1-triacetyl-*d*-xylosidopyrimidine in 50 cc. of warm absolute ethyl alcohol was treated with 20 cc. of alcohol containing 2 cc. of liquid ammonia. On cooling the solution to room temperature, the acetyl compound separated but redissolved gradually within several hours. After two days, the solution was concentrated under diminished pressure; the resulting colorless residue rapidly crystallized when agitated. It was recrystallized from 50 cc. of absolute ethyl alcohol and separated as large stout rods; the yield was practically quantitative. The product sintered at 206° and melted at 208°; it resolidified on

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(7) Hilbert and Johnson, THIS JOURNAL, **52**, 2001 (1930).

(8) Hilbert and Jansen, *ibid.*, **58**, 60 (1936).

(9) This was prepared from *d*-xylose which was kindly donated by W. E. Emery, Chief, Organic and Fibrous Materials Division, Bureau of Standards.

(10) Levene and Raymond, *J. Biol. Chem.*, **90**, 247 (1931).

(11) *l*-Arabinose was a gift from Professor J. J. Donleavy of Yale University.

(12) Hudson, Sci. Papers Bur. of Stand. (U. S. Dept. of Commerce) No. 533, 350 (1926).

(13) Chavanne, *Compt. rend.*, **134**, 661 (1902).

(14) All melting points are corrected.

(15) Fischer and Armstrong [*Ber.*, **35**, 838 (1902)] report 82–83°; and Ohle, Marecek and Bourjau [*ibid.*, **62**, 846 (1929)] report 85°.

cooling and then melted again at 208°; $[\alpha]^{23}\text{D}$ +47.9° (c = 4.64 in distilled water). This xylosido derivative is very soluble in cold water, slightly soluble in hot alcohol and insoluble in non-polar solvents.

Anal. Calcd. for $C_{11}H_{16}O_6N_2$: C, 48.50; H, 5.93; N, 10.29; OC_2H_5, 16.55. Found: C, 48.58; H, 5.83; N, 10.39; OC_2H_5, 16.17.

1-*d*-Xylosidouracil.—To a solution of 4 g. of 1,2-dihydro-2-keto-4-ethoxy-1-triacetyl-*d*-xylosidopyrimidine in 65 cc. of hot absolute methanol was added 10 cc. of methanol containing 26% by weight of hydrogen chloride. After standing for three days, the clear solution was concentrated under diminished pressure and the residual sirup rapidly crystallized. The solid cake was broken up, triturated with alcohol and filtered; yield 2.35 g. It was recrystallized from 60 cc. of 90% ethyl alcohol, separating as distorted octahedra, which were anhydrous; sintered 243°, m. p. 245°; $[\alpha]^{24}\text{D}$ +21.8° (c = 1.46 in distilled water). On another occasion it separated as long silky needles containing 8.5% solvent of crystallization (slowly removed at the boiling point of xylene *in vacuo*). 1-*d*-Xylosidouracil is much less soluble in water than other pyrimidine nucleosides; about 30 cc. of water was required to dissolve 1 g. at room temperature.

Anal. Calcd. for $C_9H_{12}O_6N_2$: C, 44.24; H, 4.95; N, 11.48. Found: C, 44.42; H, 4.74; N, 11.39.

1,2 - Dihydro - 2 - keto - 4 - ethoxy - 1 - tetraacetyl - *d* - galactosidopyrimidine.—A solution of 40 g. of acetobromo-*d*-galactose and 40 g. of 2,4-diethoxypyrimidine was heated at 65° for twenty-one hours. The reaction mixture consisted of a pale brown sirup and a small amount (0.1 g.) of uracil. After adding an equal volume of dry ether, it was filtered and the filtrate placed in the ice-chest overnight. A crystalline cake separated, which was broken up, filtered and washed with ether; yield 16.7 g. (the yield based on acetobromo-*d*-galactose was 37%, or based on 2,4-diethoxypyrimidine 15% of the theoretical). It was recrystallized from 95% ethyl alcohol and separated as plates which when desolvated sintered at 156° and melted at 159°; $[\alpha]^{21}\text{D}$ +59.2° (c = 5.53 in U. S. P. chloroform). The amount of solvent of crystallization present in the crystals varied with the conditions of crystallization; for example, the loss in weight of air-dried specimens obtained from three different crystallizations was 5.0, 5.6 and 6.3%. The ethoxyl content of the air-dried specimen, which lost 5.6% by weight when heated *in vacuo*, was determined by analysis; found, 12.0, thus indicating that a portion of the solvent of crystallization is ethyl alcohol. After drying at 61° to constant weight it was analyzed.

Anal. Calcd. for $C_{20}H_{26}O_{11}N_2$: C, 51.04; H, 5.57; N, 5.96; OC_2H_5, 9.53. Found: C, 51.26; H, 5.90; N, 6.14; OC_2H_5, 9.47.

1 - *d* - Galactosidouracil.—1,2 - Dihydro - 2 - keto - 4 - ethoxy-1-tetraacetyl-*d*-galactosidopyrimidine was simultaneously deacetylated and deëthylated in the same manner as that described for the preparation of 1-*d*-xylosidouracil. The galactoside was recrystallized from 80% ethyl alcohol and deposited on cooling as thick rhombs; s. p. 235°; m. p. 250–251°; $[\alpha]^{25}\text{D}$ +59.9° (c = 5.01 in distilled water). It was soluble in an equal weight of boiling water and crystallized on cooling.

Anal. Calcd. for $C_{10}H_{14}O_7N_2$: C, 43.80; H, 5.11; N 10.22. Found: C, 43.47; H, 5.33; N, 10.21.

1,2 - Dihydro - 2 - keto - 4 - ethoxy - 1 - triacetyl - *l* - arabinosidopyrimidine.—Two grams of finely divided acetobromo-*l*-arabinose and 2 cc. of 2,4-diethoxypyrimidine were heated at 70° for nineteen hours. Acetobromo-*l*-arabinose was not very soluble in warm 2,4-diethoxypyrimidine and the mixture was frequently shaken to facilitate solution. The end-product of the reaction was a clear light brown sirup. It was dissolved in an equal volume of ether and placed in the ice-chest for one week as crystallization took place very slowly. The crystalline material was separated and washed well with ether; yield 0.90 g. (38% of the theoretical yield based on the acetobromo-*l*-arabinose). It was dissolved in hot ethyl alcohol, ether added and the solution cooled; the crystals separated without solvent of crystallization; $[\alpha]^{21}\text{D}$ +108.8° (c = 4.11 in U. S. P. chloroform).

Anal. Calcd. for $C_{17}H_{22}O_9N_2$: C, 51.23; H, 5.57; N, 7.04. Found: C, 51.35; H, 5.56; N, 7.12.

This arabinose derivative was dimorphous; when its alcoholic solution was chilled rapidly it had a tendency to separate as needles; m. p. 157°. When the solution was cooled very slowly it generally crystallized as huge monoclinic prisms; m. p. 167.5°. Apparently the latter was the stable form as the mixed melting point of the two was 167.5°. The melt sometimes crystallized in the unstable form and at other times in the stable form.

1-*l*-Arabinosidouracil was prepared in an analogous manner to that described for the preparation of 1-*d*-xylosidouracil. The sirup obtained after concentrating the alcoholic hydrochloric acid solution crystallized when treated with alcohol (frequent vigorous stirring); yield, practically quantitative. After crystallization from 90% ethyl alcohol from which it separated as diamond-shaped hexahedra it melted at 251–252°; $[\alpha]^{23}\text{D}$ +88.2° (c = 1.21 in distilled water).

Anal. Calcd. for $C_9H_{12}N_2O_6$: C, 44.24; H, 4.95; N, 11.48. Found: C, 44.40; H, 5.00; N, 11.51.

Some By-products Formed in the Interaction of Acetobromoglycosides with 2,4-Diethoxypyrimidine

1,2 - Dihydro - 2 - keto - 1 - ethyl - 4 - ethoxypyrimidine was isolated from the reaction mixtures in which the reactants with 2,4-diethoxypyrimidine were acetobromo-*d*-glucose, acetobromo-*d*-xylose and acetobromo-*d*-mannose. The manner in which it was obtained was the following one. After filtering the nucleoside that crystallized from the solution of the reaction sirup in ether, the filtrate was set in a refrigerator. The separation of 1,2-dihydro-2-keto-1-ethyl-4-ethoxypyrimidine was very slow, generally requiring several days. The solid product, after filtering and washing with ether, was quite sticky and was purified by sublimation (long plates); yield 4 g.[16] from 50 g. of acetobromo-*d*-glucose and 50 g. of 2,4-diethoxypyrimidine. It was recrystallized from ether as stout needles of m. p.

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[16] This represents only a fraction of the product present in the reaction mixture. 1,2-Dihydro-2-keto-1-ethyl-4-ethoxypyrimidine can be removed quantitatively by extracting the ether solution of the original filtered sirup with water. This procedure was not adopted since it was desired to avoid the hydrolysis of and to isolate if possible "orthoacetates" or products in which the sugar was attached to the 2-position of the pyrimidine ring.

88°. This 1-ethyl derivative is very soluble in cold water, alcohol, and chloroform and slightly soluble in ether; it does not give a Wheeler–Johnson color test.

Anal. Calcd. for $C_8H_{12}O_2N_2$: C, 57.10; H, 7.20; N, 16.67. Found: C, 57.21; H, 7.13; N, 16.58.

1-Ethyluracil.—This was obtained by dissolving the above compound (1.00 g.) in concentrated hydrochloric acid (10 cc.) and concentrating to dryness on a steam-bath. The residue was crystallized from a solution of alcohol and ether and separated as clusters of prisms; m. p. 147.5°; yield 0.53 g. 1-Ethyluracil is very soluble in cold water, alcohol and acetone, slightly soluble in ether and sparingly soluble in hot carbon tetrachloride; it did not give a Wheeler–Johnson color test.

Anal. Calcd. for $C_6H_8O_2N_2$: C, 51.40; H, 5.76; N, 20.00. Found: C, 51.61; H, 5.75; N, 20.14.

1,2 - Dihydro - 2 - keto - 4 - ethoxypyrimidine was isolated from the products formed in the interaction of either acetobromo-*d*-mannose or acetobromo-*d*-galactose with 2,4-diethoxypyrimidine. As the methods of isolating the material in the two cases was quite similar only the details of the procedure, in which the former sugar was used, will be described. A solution of 7 g. of acetobromo-*d*-mannose and 7 g. of 2,4-diethoxypyrimidine was heated at 65° for seventy hours; after cooling a small amount of uracil deposited and this was removed. From the filtrate, 1,2-dihydro-2-keto-1-ethyl-4-ethoxypyrimidine (2 g.) slowly crystallized and after a week it was collected. The sirupy filtrate over a period of a year slowly deposited a crystalline product. The solid was removed by filtration and washed with a small amount of ether. Trituration with chloroform separated the ethoxy derivative from uracil. The chloroformic extract was concentrated and the residue recrystallized from a solution containing 90% benzene and 10% absolute ethyl alcohol; massive aggregates of colorless plates were thus obtained; yield 0.36 g.; m. p. 168°; a mixed melting point with 1,2-dihydro-2-keto-4-ethoxypyrimidine[17] was unchanged. The properties as well as the response to the Wheeler–Johnson color test are identical with those described previously for this compound.

Anal. Calcd. for $C_6H_8O_2N_2$: C, 51.40; H, 5.76; N, 20.00. Found: C, 51.75; H, 5.76; N, 19.95.

Uracil was isolated in traces in all experiments except when acetobromo-*d*-glucose was used. This pyrimidine was easily obtained in the pure state by triturating the crude material with chloroform and then recrystallizing from water; it was identified by its properties, Wheeler–Johnson color test and analysis.

Summary

Acetobromoglycosides, in general, interact with 2,4-diethoxypyrimidine to give 1,2-dihydro-2-keto-1-acetylglycosido-4-ethoxypyrimidines. Appreciable amounts of the secondary product, 1,2-dihydro-2-keto-1-ethyl-4-ethoxypyrimidine are also formed. Presumptive evidence indicates that by-products, structurally related to the 4-ethoxy-2-triacetyl-*d*-ribosidopyrimidine which is formed in the interaction of acetobromo-*d*-ribose and 2,4-diethoxypyrimidine, are present in the products of the reaction of 2,4-diethoxypyrimidine with acetobromo-*d*-mannose and with acetobromo-*d*-galactose; however, attempts to isolate these analogs in the crystalline condition have thus far been unsuccessful. Hydrolysis of 1-acetylglycosidopyrimidine derivatives with alcoholic hydrochloric acid produces the 1-glycosidouracils. 1-*d*-Xylosido-, 1-*l*-arabinosido- and 1-*d*-galactosidouracil were prepared in this manner and their chemical properties found to be similar to those of uridine.

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[17] Hilbert and Jansen, THIS JOURNAL, **57**, 552 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conductivities of One-Molal Mixtures of Alkali Halides and Nitrates

BY PIERRE VAN RYSSELBERGHE AND LEE NUTTING

Introduction

As pointed out by Smith and Gortner,[1] few systematic studies of the conductivity of mixed electrolytes are available for theoretical investigation. Moreover, the available data have not as yet received an entirely satisfactory interpretation. The small but definite departures from the mixture rule observed by Stearn and by Ruby and Kawai[2] in the case of mixed alkali halides have recently been discussed by Van Rysselberghe and Nutting.[3] They showed that these departures could be reduced appreciably if the mixture rule is corrected by means of simple but plausible assumptions concerning the adjustment of mobilities which takes place upon mixing. The modified form of the mixture rule obtained by them involves the transport numbers of the ions in solutions of the pure salts. As these transport numbers are not always known with great accuracy calculations of real significance cannot be carried

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[1] Smith and Gortner, *J. Phys. Chem.*, **37**, 79 (1933).

[2] Stearn, THIS JOURNAL, **44**, 670 (1922); Ruby and Kawai, *ibid.*, **48**, 1119 (1926).

[3] Van Rysselberghe and Nutting, *ibid.*, **56**, 1435 (1934).

TABLE I

DENSITIES AND CONDUCTIVITIES OF 1 MOLAL MIXTURES OF ALKALI HALIDES AND NITRATES

Molality	Density	Specific conductivity	Equivalent conductivity		ΔΛ
			Measured	Calculated	
		1. LiCl + KI			
1 LiCl	1.0202	0.07198	73.54		
$^{3}/_{4}$ LiCl + $^{1}/_{4}$ KI	1.0433	.08174	84.09	84.80	−0.71
$^{1}/_{2}$ LiCl + $^{1}/_{2}$ KI	1.0660	.09178	95.08	96.00	− .92
$^{1}/_{4}$ LiCl + $^{3}/_{4}$ KI	1.0884	.10226	106.66	107.31	− .65
1 KI	1.1106	.11292	118.56		
		2. NaCl + KI			
1 NaCl	1.0360	0.08439	86.21		
$^{3}/_{4}$ NaCl + $^{1}/_{4}$ KI	1.0550	.09120	93.83	94.30	−0.47
$^{1}/_{2}$ NaCl + $^{1}/_{2}$ KI	1.0735	.09810	101.64	102.38	− .74
$^{1}/_{4}$ NaCl + $^{3}/_{4}$ KI	1.0923	.10542	109.94	110.47	− .53
1 KI	1.1106	.11292	118.56		
		3. KCl + KI			
1 KCl	1.0414	0.10861	112.06		
$^{3}/_{4}$ KCl + $^{1}/_{4}$ KI	1.0589	.10963	113.62	113.68	−0.06
$^{1}/_{2}$ KCl + $^{1}/_{2}$ KI	1.0762	.11064	115.18	115.31	− .13
$^{1}/_{4}$ KCl + $^{3}/_{4}$ KI	1.0934	.11179	116.88	116.93	− .05
1 KI	1.1106	.11292	118.56		
		4. KCl + NaI			
1 KCl	1.0414	0.10861	112.06		
$^{3}/_{4}$ KCl + $^{1}/_{4}$ NaI	1.0575	.10346	106.97	106.97	0.00
$^{1}/_{2}$ KCl + $^{1}/_{2}$ NaI	1.0735	.09826	101.85	101.88	− .03
$^{1}/_{4}$ KCl + $^{3}/_{4}$ NaI	1.0890	.09295	96.54	96.80	− .26
1 NaI	1.1059	.08820	91.71		
		5. NaCl + KNO$_3$			
1 NaCl	1.0360	0.08439	86.21		
$^{9}/_{10}$ NaCl + $^{1}/_{10}$ KNO$_3$	1.0379	.08351	87.35	86.87	+0.48
$^{3}/_{4}$ NaCl + $^{1}/_{4}$ KNO$_3$	1.0409	.08674	89.09	87.87	+1.22
$^{1}/_{2}$ NaCl + $^{1}/_{2}$ KNO$_3$	1.0455	.08841	91.31	89.52	+1.79
$^{1}/_{4}$ NaCl + $^{3}/_{4}$ KNO$_3$	1.0504	.08897	92.36	91.17	+1.19
$^{1}/_{10}$ NaCl + $^{9}/_{10}$ KNO$_3$	1.0530	.08903	92.73	92.17	+0.56
1 KNO$_3$	1.0551	.08895	92.83		
		6. KCl + KNO$_3$			
1 KCl	1.0414	0.10861	112.06		
$^{9}/_{10}$ KCl + $^{1}/_{10}$ KNO$_3$	1.0425	.10659	110.14	110.13	+0.01
$^{3}/_{4}$ KCl + $^{1}/_{4}$ KNO$_3$	1.0446	.10343	107.05	107.25	− .20
$^{1}/_{2}$ KCl + $^{1}/_{2}$ KNO$_3$	1.0482	.09843	102.14	102.44	− .30
$^{1}/_{4}$ KCl + $^{3}/_{4}$ KNO$_3$	1.0515	.09367	97.50	97.63	− .13
$^{1}/_{10}$ KCl + $^{9}/_{10}$ KNO$_3$	1.0534	.09086	94.74	94.76	− .02
1 KNO$_3$	1.0551	.08895	92.83		
		7. NaCl + NaNO$_3$			
1 NaCl	1.0360	0.08439	86.21		
$^{9}/_{10}$ NaCl + $^{1}/_{10}$ NaNO$_3$	1.0373	.08304	84.95	85.23	−0.28
$^{3}/_{4}$ NaCl + $^{1}/_{4}$ NaNO$_3$	1.0396	.08148	83.48	83.75	− .27
$^{1}/_{2}$ NaCl + $^{1}/_{2}$ NaNO$_3$	1.0431	.07887	81.04	81.28	− .24
$^{1}/_{4}$ NaCl + $^{3}/_{4}$ NaNO$_3$	1.0466	.07635	78.67	78.82	− .15
$^{1}/_{10}$ NaCl + $^{9}/_{10}$ NaNO$_3$	1.0485	.07480	77.21	77.34	− .13
1 NaNO$_3$	1.0497	.07387	76.36		
		8. KCl + NaNO$_3$			
1 KCl	1.0414	0.10861	112.06		
$^{9}/_{10}$ KCl + $^{1}/_{10}$ NaNO$_3$	1.0419	.10415	107.52	108.49	−0.97
$^{3}/_{4}$ KCl + $^{1}/_{4}$ NaNO$_3$	1.0433	.09761	100.77	103.13	−2.36
$^{1}/_{2}$ KCl + $^{1}/_{2}$ NaNO$_3$	1.0456	.08841	91.30	94.21	−2.91
$^{1}/_{4}$ KCl + $^{3}/_{4}$ NaNO$_3$	1.0479	.08038	83.03	85.28	−2.25
$^{1}/_{10}$ KCl + $^{9}/_{10}$ NaNO$_3$	1.0493	.07629	78.81	79.93	−1.12
1 NaNO$_3$	1.0497	.07387	76.36		

TABLE I (*Concluded*)

Molality	Density	Specific conductivity	Equivalent conductivity Measured	Equivalent conductivity Calculated	ΔΛ
		9. $KNO_3 + NaNO_3$			
1 KNO_3	1.0551	0.08895	92.83		
$^3/_4$ KNO_3 + $^1/_4$ $NaNO_3$	1.0537	.08491	88.41	88.71	−0.30
$^1/_2$ KNO_3 + $^1/_2$ $NaNO_3$	1.0525	.08108	84.21	84.59	− .38
$^1/_4$ KNO_3 + $^3/_4$ $NaNO_3$	1.0512	.07737	80.15	80.48	− .35
1 $NaNO_3$	1.0497	.07387	76.36		

out in all cases. In this paper we present a series of data obtained with mixtures of alkali halides and alkali nitrates of total molality one. These data are compared with the values derived from the simple, uncorrected mixture rule.

Experimental

A complete description of the circuit used in this work has been given elsewhere by Nutting.[4] One feature of the method is the use of a vacuum tube oscillator as a source of alternating current. A frequency of 1000 ± 5 cycles was obtained by calibrating the oscillator against a 1000 cycle tuning fork. To facilitate the determination of the point at which the bridge was in balance, a two-stage audiofrequency amplifier was used. Comparative tests with a Grinnell Jones bridge used in this Laboratory for other purposes gave satisfactory results. The accuracy of the resistance measurements was estimated at ±0.05%.

The conductivity cell was similar in design to that proposed by McBain, Laing and Titley.[5] A detailed study of the variation of cell constant was made in connection with the present measurements and others to be reported later. Observations in general agreement with those of Jones and Bollinger[6] were made and the true value of the cell constant was obtained for each resistance through an extensive series of measurements involving the various Kohlrausch solutions (prepared according to "I. C. T.," Vol. VI, p. 230) and a number of solutions of single salts for which reliable data are available in the literature. A water thermostat (later replaced by an oil one without any noticeable change in the slight temperature fluctuations nor in the measured resistances) kept the temperature within 25 ± 0.02°.

Salts of the highest purity were used (Kahlbaum, für Analyse; Merck, Reagent, analyzed; Baker, C. P. analyzed). Water of specific conductance consistently lower than 2×10^{-6} was used throughout, but no correction was necessary as all our specific conductances were of the order of 10^{-1} and the accuracy was estimated at ±0.15%. Our results with pure salts compare quite well with those of Stearn and of Ruby and Kawai (for 1 molal KCl, S. finds 111.50; R. and K. find 112.29; we find 112.06; for 1 molal NaCl, S. finds 86.36; R. and K. find 86.07; we find 86.21).

The results are reported in Table I. The densities, specific and equivalent conductivities are given in columns 2 to 4. In column 5 we give the values computed by the ordinary mixture rule and in column 6 the differences ΔΛ between the experimental and theoretical values.

Discussion

The differences between measured and calculated values are in all cases quite definite but regularities are difficult to detect. It can be seen that in most cases the departure from the mixture rule is the larger, the larger the difference between the conductivities of the pure salts. There are, however, conspicuous exceptions (mixtures of sodium chloride and potassium nitrate and mixtures of potassium chloride and sodium nitrate). In Table II we have arranged the various mixtures studied by us and the 1-molal mixtures of NaCl + KCl, NaBr + KBr, NaI + KI studied by Stearn in the order corresponding to decreasing differences between the conductivities of the pure salts. For each pair of salts we give this difference (λ) and the maximum deviation between measured and calculated conductivities (ΔΛ) for the intermediate mixtures. There is a rough parallelism between these two quantities (if the KCl + $NaNO_3$ and the NaCl + KNO_3 mixtures are left out of consideration). A similar parallelism holds at the other total concentrations for which data are available. The mixture rule is thus more nearly correct when the mobilities of the component ions are only slightly different from one another in solutions of the pure salts. The mobilities in the mixtures will then differ but little from their values in solutions of the pure salts. When mobilities are quite different, the adjustment which has to take place upon mixing is less likely

TABLE II

Mixtures	λ	ΔΛ
LiCl + KI	45.02	−0.92
KCl + $NaNO_3$	35.70	−2.91
NaCl + KI	32.35	−0.74
NaBr + KBr	26.60	− .60
NaI + KI	26.05	− .65
NaCl + KCl	25.24	− .63
KCl + NaI	20.35	− .26
KCl + KNO_3	19.23	− .30
KNO_3 + $NaNO_3$	16.47	− .38
NaCl + $NaNO_3$	9.85	− .24
NaCl + KNO_3	6.62	+1.79
KCl + KI	6.50	−0.13

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[4] Nutting, *J. Chem. Educ.*, **12**, 286 (1935).

[5] McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1279 (1919).

[6] Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

to lead to satisfactory agreement with the mixture rule. When large departures are observed, as in the case of solutions containing simultaneously the ions Na^+, K^+, Cl^-, NO_3^-, some specific effect is probably present and its cause may be due to slightly incomplete dissociation of one of the salts present. Outside of these exceptional cases, the regularities which we have just discussed hold whether the salts have a common ion or not.

The application of the mixture rule to solutions of a given molality rather than to solutions of a given molar concentration has been quite customary. We have found that the departures between measured and calculated conductivities are of the same order of magnitude in both scales of concentration.

Summary

1. The densities and the conductivities of nine pairs of alkali halides and nitrates have been measured at a total concentration of one-molal.

2. The mixture rule has been found to be more nearly correct when the component salts have conductivities which differ but slightly.

3. Attention has been called to the wide discrepancies between measured and calculated conductivities in the case of solutions containing simultaneously the ions Na^+, K^+, Cl^- and NO_3^-.

STANFORD UNIVERSITY, CALIF.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conductivities of Concentrated Binary Mixtures of Electrolytes with a Common Anion and at Least One Ion of Charge Two

BY PIERRE VAN RYSSELBERGHE, S. W. GRINNELL AND J. M. CARLSON

Introduction

In the foregoing paper, Van Rysselberghe and Nutting[1] have shown, in general agreement with previous results of Stearn and of Ruby and Kawai,[2] that mixtures of 1-1 salts exhibit but small departures from the mixture rule, with the exception of mixtures containing simultaneously the Na^+, K^+, Cl^- and NO_3^- ions for which the departure is sometimes larger than 2 conductivity units. The results seem to show that there is a rough parallelism between the maximum departure from the mixture rule observed for a series of mixtures of a given total concentration and the difference between the conductivities of the pure salts at this same concentration.

In the case of mixtures containing ions of higher valence Smith and Gortner[3] observed departures as large as 7 conductivity units on a Λ of about 120 at concentrations as low as 0.01 N. In the present investigation we have studied mixtures for which extreme departures from the mixture rule were observed (cadmium halides + potassium halides) and others for which large departures were expected but were actually found to be small (magnesium chloride + alkali halides). Other cases are of an intermediate type. Some of these mixtures have been studied previously in a less systematic manner from the point of view of complex ion formation. This older literature is reviewed in various monographs such as that of Walden.[4] The interpretation given by the various authors is based upon the Arrhenius theory and should be carefully revised.

Experimental

The method followed in the present work is essentially the same as that used by Van Rysselberghe and Nutting.[1] Solutions were prepared on a volume concentration basis by means of calibrated glassware. The salts used were of the highest possible purity (Baker C. P. Analyzed, Merck reagent analyzed, Kahlbaum für Analyse). Several of these salts, however, are very hygroscopic, others decompose upon drying at temperatures above 120° and, although all the usual precautions were taken, the accuracy is in several cases less than ±0.5% on the absolute value of the conductivity. Mixtures were prepared by mixing solutions of the pure salts. Conductivities of the pure salts were measured several times, each time with a freshly prepared solution, and were found to be at least as accurate as the data available in "I. C. T." or in the Landolt-Börnstein-Roth Tables. The temperature was in all cases 25 ± 0.02°. In Table I we give the measured specific conductivity, the measured equivalent conductivity, the equivalent conductivity as deduced from the mixture

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[1] Van Rysselberghe and Nutting, THIS JOURNAL, **59**, 333 (1937).

[2] Stearn, *ibid.*, **44**, 670 (1922); Ruby and Kawai, *ibid.*, **48**, 1119 (1926).

[3] Smith and Gortner, *J. Phys. Chem.*, **37**, 79 (1933).

[4] Walden, "Das Leitvermögen der Lösungen," in "Handbuch der allgemeinen Chemie," Akademische Verlagsgesellschaft, Leipzig, Vol. IV, Part II, 1924, pp. 257-262.

rule and the difference ΔΛ between measured and calculated conductivities for a series of mixtures of cadmium iodide and potassium iodide. Several of these mixtures correspond to the composition $CdI_2 \cdot KI$ for which data were so far not available. Conductivities of mixtures corresponding to the composition $CdI_2 \cdot 2KI$ are given in the literature.

TABLE I

CONDUCTIVITIES OF MIXTURES OF CdI_2 AND KI AT 25°

Composition Equivalents per liter CdI_2	KI	Specific conductivity	Equivalent conductivity measured	Equivalent conductivity calculated	ΔΛ
1.0	0	0.01781	17.81		
1.0	0.1	.02442	22.20	26.3	− 4.1
1.0	.2	.03132	26.10	33.6	− 7.5
1.0	.3	.03834	29.53	39.6	−10.1
1.0	.5	.05289	35.26	49.1	−13.8
1.0	.8	.07677	42.65	59.0	−16.4
1.0	1.0	.09419	47.09	64.0	−16.9
1.0	1.5	.14413	57.65	71.7	−14.1
1.0	2.0	.19365	64.55	76.0	−11.5
1.0	3.0	.28422	71.05	79.0	− 7.9
1.0	4.0	.35998	72.00	76.1	− 4.1
0.2	0.1	.01423	47.42	58.3	−10.9
.6	.3	.03477	38.63	51.7	−13.1
1.0	.5	.05289	35.26	49.1	−13.8
1.6	.8	.07645	31.85	46.0	−14.2
2.0	1.0	.09001	30.00	43.8	−13.8
0.2	1.0	.11528	96.07	100.5	− 4.4
.4	1.0	.11179	79.85	87.6	− 7.7
1.0	1.0	.09419	47.09	64.0	−16.9
2.0	1.0	.09001	30.00	43.8	−13.8

In order to follow the trend of ΔΛ in each series, the data for three mixtures (1 CdI_2 + 0.5 KI, 1 + 1, 2 + 1) are given twice in the table. The conductivities of the pure salts, used in the calculated Λ's, were taken from smooth curves obtained by plotting all the data available in the literature.

In Table II we give the conductivities of eight groups of mixtures arranged in series corresponding to the same total equivalent concentration. We represent by x and $1 - x$ the fractions of the total equivalent concentration corresponding to salts 1 and 2, salt 1 being the first in the title of the series. Some of the data given for the CdI_2 + KI mixtures were obtained from curves drawn by means of the data of Table I.

TABLE II

CONDUCTIVITIES OF CONCENTRATED MIXTURES AT 25°

Composition x	$1 - x$	Specific conductivity	Equivalent conductivity Measured	Equivalent conductivity Calculated	−ΔΛ
		1.1 0.5 *N* mixtures of CdI_2 + KI			
1	0		21.4		
2/3	1/3		43.8	54.8	11.0
1/2	1/2		56.8	71.5	14.7
1/4	3/4	0.04355	87.10	96.6	9.5
0	1	.06083	121.66		
		1.2 1 *N* mixtures of CdI_2 + KI			
1	0	0.01781	17.81		
11/12	1/12	.02230	22.30	26.12	3.82
2/3	1/3		38.0	51.02	13.0
1/2	1/2		51.6	67.64	16.0
1/4	3/4		83.5	92.56	9.1
1/8	7/8	.10001	100.01	104.98	4.97
0	1	.11746	117.46		
		1.3 2 *N* mixtures of CdI_2 + KI			
1	0	0.02835	14.18		
2/3	1/3		33.2	47.4	14.2
1/2	1/2	.09419	47.1	63.9	16.8
0	1	.2274	113.7		
		2.1 1 *N* mixtures of $CdBr_2$ + KBr			
1	0	0.02109	21.09		
5/6	1/6	.03396	33.96	37.08	3.12
2/3	1/3	.04606	46.06	53.06	7.00
1/2	1/2	.05930	59.30	69.05	9.75
1/3	2/3	.07620	76.20	85.03	8.83
0	1	.11701	117.01		
		2.2 2 *N* mixtures of $CdBr_2$ + KBr			
1	0	0.02909	14.54		
5/6	1/6	.05195	25.97	30.58	4.61
2/3	1/3	.07109	35.54	46.61	11.07
1/2	1/2	.10114	50.57	62.64	12.07
1/3	2/3	.13601	68.00	78.68	10.68
0	1	.2215	110.75		
		3.1 1 *N* mixtures of $CdCl_2$ + KCl			
1	0	0.02264	22.64		
5/6	1/6	.03417	34.17	35.86	1.69
2/3	1/3	.04739	47.39	52.40	5.01
1/2	1/2	.06161	61.61	67.27	5.66
1/3	2/3	.07717	77.17	82.15	4.98
1/6	5/6	.09444	94.44	97.02	2.58
0	1	.11190	111.90		
		3.2 2 *N* mixtures of $CdCl_2$ + KCl			
1	0	0.02820	14.10		
5/6	1/6	.04903	24.51	29.34	4.83
2/3	1/3	.07453	37.26	44.58	7.32
1/2	1/2	.10329	51.64	59.81	8.17
1/3	2/3	.13601	68.00	75.05	7.05
1/6	5/6	.17292	86.46	90.29	3.83
0	1	.21106	105.53		
		4.1 1 *N* mixtures of ZnI_2 + KI			
1	0	0.07823	78.23		
2/3	1/3	.09007	90.07	91.30	1.23
1/2	1/2	.09637	96.37	97.84	1.47
1/3	2/3	.10362	103.62	104.37	0.75
1/6	5/6	.11097	110.97	110.92	−0.05
0	1	.11746	117.46		
		4.2 2 *N* mixtures of ZnI_2 + KI			
1	0	0.12333	61.66		
2/3	1/3	.15422	77.11	78.62	1.51
1/2	1/2	.16986	84.93	87.10	2.17
1/3	2/3	.18743	93.71	95.57	2.86
1/6	5/6	.20644	103.22	104.06	0.84
1	0	.22507	112.53		

TABLE II (*Concluded*)

Composition x	$1-x$	Specific conductivity	Equivalent conductivity Measured	Equivalent conductivity Calculated	$-\Delta\Lambda$
		4.3 4 N mixtures of ZnI_2 + KI			
1	0	0.11814	29.55		
5/6	1/6	.1519	37.97	41.34	3.37
2/3	1/3	.1872	46.80	53.16	6.36
1/2	1/2	.2326	58.15	64.99	6.84
1/3	2/3	.2807	70.17	76.81	6.64
1/6	5/6	.3343	83.57	88.62	5.05
0	1	.4018	100.45		
		4.4 6 N mixtures of ZnI_2 + KI			
1	0	0.0833	13.88		
5/6	1/6	.1229	20.48	25.18	4.70
2/3	1/3	.1691	28.18	36.48	8.30
1/2	1/2	.2367	39.45	47.78	8.33
1/3	2/3	.3093	51.55	59.08	7.53
1/6	5/6	.4079	67.98	70.38	2.40
0	1	.4901	81.68		
		5.1 1 N mixtures of $CdSO_4$ + K_2SO_4			
1	0	0.02852	28.52		
5/6	1/6	.03510	35.10	37.40	2.30
2/3	1/3	.04328	43.28	46.27	2.99
1/2	1/2	.05185	51.85	55.15	3.30
1/3	2/3	.06108	61.08	64.03	2.95
1/6	5/6	.07104	71.04	72.90	1.86
0	1	.08178	81.78		
		6.1 2 N mixtures of $CdSO_4$ + $MgSO_4$			
1	0	0.04350	21.75		
5/6	1/6	.04462	22.31	22.31	0.00
2/3	1/3	.04575	22.87	22.86	− .01
1/2	1/2	.04691	23.45	23.42	− .03
1/3	2/3	.04791	23.95	23.97	.02
1/6	5/6	.04903	24.51	24.53	.02
0	1	.05018	25.09		
		6.2 4 N mixtures of $CdSO_4$ + $MgSO_4$			
1	0	0.05486	13.71		
5/6	1/6	.05527	13.82	13.78	−0.04
2/3	1/3	.05589	13.97	13.86	− .11
1/2	1/2	.05621	14.05	13.99	− .06
1/3	2/3	.05661	14.15	14.01	− .14
1/6	5/6	.05684	14.21	14.08	− .13
0	1	.05711	14.28		
		7.1 1 N mixtures of $MgCl_2$ + NaCl			
1	0	0.07177	71.77		
5/6	1/6	.07390	73.90	74.13	0.23
2/3	1/3	.07628	76.28	76.56	.28
1/2	1/2	.07869	78.69	79.02	.33
1/3	2/3	.08091	80.91	81.42	.51
1/6	5/6	.08357	83.57	83.85	.28
0	1	.08628	86.28		
		7.2 2 N mixtures of $MgCl_2$ + NaCl			
1	0	0.11714	58.57		
5/6	1/6	.12230	61.15	61.30	0.15
2/3	1/3	.12749	63.74	64.03	.27
1/2	1/2	.13319	66.59	66.75	.16
1/3	2/3	.13857	69.28	69.48	.20
1/6	5/6	.14422	72.11	72.21	.10
0	1	.14986	74.93		
		7.3 4 N mixtures of $MgCl_2$ + NaCl			
1	0	0.15935	39.84		
5/6	1/6	.17011	42.53	42.66	0.13
2/3	1/3	.18102	45.25	45.89	.64
1/2	1/2	.19276	48.19	48.76	.57
1/3	2/3	.20484	51.21	51.94	.73
1/6	5/6	.21732	54.33	54.96	.63
0	1	.23077	57.69		
		7.4 5 N mixtures of $MgCl_2$ + NaCl			
1	0	0.16187	32.37		
5/6	1/6	.17462	34.92	35.28	0.36
2/3	1/3	.18822	37.64	38.18	.54
1/2	1/2	.20219	40.44	41.09	.65
1/3	2/3	.21686	43.37	43.99	.62
1/6	5/6	.23287	46.57	46.90	.33
0	1	.24906	49.81		
		8.1 5 N mixtures of $MgCl_2$ + LiCl			
1	0	0.16187	32.37		
5/6	1/6	.16603	33.21	33.25	0.04
2/3	1/3	.17008	34.02	34.13	.11
1/2	1/2	.17456	34.91	35.01	.10
1/3	2/3	.17894	35.79	35.89	.10
1/6	5/6	.18352	36.70	36.77	.07
0	1	.18823	37.65		
		8.2 9 N mixtures of $MgCl_2$ + LiCl			
1	0	0.10386	11.54		
5/6	1/6	.11120	12.36	12.44	0.08
2/3	1/3	.11864	13.18	13.34	.16
1/2	1/2	.12538	13.93	14.23	.30
1/3	2/3	.13448	14.94	15.13	.19
1/6	5/6	.14337	15.93	16.03	.10
0	1	.15236	16.93		

Discussion

If we classify the various groups of mixtures studied in the present paper according to the difference between the conductivities of the pure salts, we obtain Table III in which are given, for each type of mixture, this difference, λ, and the maximum departure from the mixture rule for the series, $\Delta\Lambda$.

If we except a few irregularities and make allowances for the experimental error, we notice a marked parallelism between λ and $\Delta\Lambda$. We consider this very simple observation as particularly significant and illuminating in view of the fact that several of the mixtures certainly contain large amounts of complex ions (CdI_3^-, $CdI_4^=$, etc.). A survey of the other data in the literature has convinced us that this parallelism is quite general, provided one excludes mixtures containing an acid and mixtures for which the sign of $\Delta\Lambda$ changes as concentration increases. Cases of this type of behavior have been reported by Smith and Gortner.[3] It seems worth mentioning that,

TABLE III

	Mixtures	λ	−ΔΛ
0.5 *N*	$CdI_2 + KI$	100.26	14.7
1 *N*	$CdI_2 + KI$	99.65	16.0
2 *N*	$CdI_2 + KI$	99.52	16.8
2 *N*	$CdBr_2 + KBr$	96.21	12.07
1 *N*	$CdBr_2 + KBr$	95.92	9.75
2 *N*	$CdCl_2 + KCl$	91.43	8.17
1 *N*	$CdCl_2 + KCl$	89.26	5.66
4 *N*	$ZnI_2 + KI$	70.92	6.84
6 *N*	$ZnI_2 + KI$	67.80	8.33
1 *N*	$CdSO_4 + K_2SO_4$	53.26	3.30
2 *N*	$ZnI_2 + KI$	50.87	2.86
1 *N*	$ZnI_2 + KI$	39.23	1.47
4 *N*	$MgCl_2 + NaCl$	17.85	0.73
5 *N*	$MgCl_2 + NaCl$	17.44	.65
2 *N*	$MgCl_2 + NaCl$	16.36	.27
1 *N*	$MgCl_2 + NaCl$	14.51	.51
9 *N*	$MgCl_2 + LiCl$	5.39	.30
5 *N*	$MgCl_2 + LiCl$	5.28	.11
2 *N*	$CdSO_4 + MgSO_4$	3.34	.03
4 *N*	$CdSO_4 + MgSO_4$	0.57	.14

for several mixtures of cadmium and zinc halides with the corresponding potassium salt, the equivalent conductivity is smaller than the contribution deduced from the mixture rule for the potassium salt alone.

Summary

1. Specific and equivalent conductivities of eight groups of binary mixtures of 2-1, 2-2 and 1-1 electrolytes with a common anion have been measured at total equivalent concentrations ranging from 0.5 to 9 *N*.

2. It is pointed out that there is a marked parallelism between the difference of the conductivities of the pure salts and the maximum departure from the mixture rule observed with the mixtures of the same total concentration.

STANFORD UNIVERSITY, CALIF.

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

Solubility. XV. The Solubility of Liquid and Solid Stannic Iodide in Silicon Tetrachloride

BY J. H. HILDEBRAND AND G. R. NEGISHI

Stannic iodide and silicon tetrachloride differ considerably in molecular size and very greatly in internal pressure or molecular field strength, so much so, indeed, that not only is the solubility of solid stannic iodide at 25° only 3% of the ideal solubility, but also in the liquid state they form two liquid phases below 140°. This system is particularly adapted to an investigation of the critical mixing phenomenon in its simplest aspects, because it is free from the complications introduced by the presence of electric dipoles or hydrogen bonds such as are present in most known cases of incomplete liquid miscibility. We have turned to it, therefore, in an effort to throw light upon the question of the extent to which the randomness of thermal mixing is affected by the tendency toward molecular clustering due to differences in the strength of intermolecular forces.[1]

The substances were prepared and purified by methods previously described.[2] The solubility of solid stannic iodide from 0 to 40° was determined by analysis of a solution saturated by shaking in a thermostat, as in earlier investigations in this Laboratory. The bulb containing a sample of saturated solution was placed, for analysis, in a thick-walled glass-stoppered 750-cc. flask containing 100 to 150 cc. of water. The air was displaced by carbon dioxide to prevent oxidation of iodide ion. The bulb was then broken and the flask shaken till the reaction was complete. The contents were transferred to a 500-cc. separatory funnel, about 25 cc. of carbon tetrachloride and a little concentrated tartaric acid solution added and the iodide ion oxidized to iodine by permanganate.[3] The iodine was extracted, separated and titrated with thiosulfate. The method proved rapid, simple and accurate. Three determinations of solubility were made at each temperature, 0.2, 25 and 40°, and the largest deviation from the mean was 0.5%.

The determinations at higher temperatures were made by the "synthetic method." The stannic iodide was introduced into each tube in a dry box, the air in the tube displaced by strongly dried and purified nitrogen and the stannic iodide melted into a single mass. The tube was then evacuated and a capillary seal broken, permitting the distillation of silicon chloride into it, after which it was sealed. The tube was weighed, both empty and after each substance had been added.

The solution temperature for each tube was determined in an oil-bath contained in a one-gallon (4-liter) unsilvered Dewar flask and heated electrically. Near the solution temperature the rate of heating was slow, 0.01° or less per

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[1] *Cf.* (a) E. A. Guggenheim, *Proc. Roy. Soc.* (London), **148A**, 304 (1935); (b) J. H. Hildebrand, *Chem. Rev.*, **18**, 315 (1936); *Trans. Faraday Soc.*, in press, "Symposium on the Liquid State" September, 1936.

[2] G. R. Negishi, THIS JOURNAL, **58**, 2293 (1936).

[3] W. C. Bray and C. M. J. Mackay, *ibid.*, **32**, 1193 (1910).

minute. The solution temperature of solid stannic iodide could be determined only with rising temperature, since supercooling occurred with falling temperature. When the stannic iodide was liquid, however, the consolute temperature was determined going in both directions, the observations agreeing within 0.05°.

The results are given in Table I.

Table I

Solubility of Stannic Iodide in Silicon Tetrachloride

t, °C.	Mole % of SnI_4		t, °C.	Mole % of SnI_4	
0.2	0.155	Solid	139.4	32.53	Liquid
25.0	.381		139.8	37.62	
40.0	.639		139.7	43.16	
81.3	2.36		139.5	43.54	
112.1	6.43		139.1	45.06	
115.6	7.40		138.8	46.95	
131.0	65.36		135.7	51.21	
130.9	21.56	Liquid	135.8	51.62	
133.4	24.21		132.4	55.12	
138.2	29.58				

The figures for the liquid–liquid portion are plotted in Fig. 1. We read the critical solution temperature and composition from this curve as 139.9° and 39 mole per cent. of stannic iodide. The results for both solid and liquid are plotted in Fig. 2 in the form of the logarithm of the mole fraction of stannic iodide against the reciprocal of the absolute temperature, as has been customary in reporting the data obtained in this Laboratory on the solubility of solids.

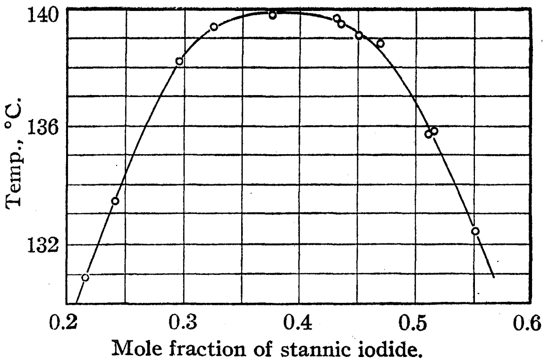

Fig. 1.—Solubility in the liquid–liquid system.

We will now examine the correlation between the curves for solid and liquid stannic iodide by applying the approximate equation[4]

$$RT \ln \frac{a_2}{N_2} = V_2\, \vartheta_1^2\, D_1^2 \qquad (1)$$

where a denotes activity in terms of the pure liquid; N, mole fraction; V, molal volume of the pure liquid; ϑ, the volume fraction of one component; and D the difference between square roots of the energy of vaporization per cc. of the pure components. The subscript 2 we shall take as referring to stannic iodide and the subscript 1 to silicon chloride. When the solution is in equilibrium with solid stannic iodide we can write $a_2 = N_2^i$, the ideal solubility, calculated from its melting point and heat of fusion by the equation

$$\log \frac{1}{N_2^i} = \frac{\Delta H}{2.303R}\,\frac{T_m - T}{T_m T} - \frac{\Delta C_p}{2.303R}\,\frac{T_m - T}{T} + \frac{\Delta C_p}{R} \log \frac{T_m}{T} \qquad (2)$$

where ΔH is the heat of fusion at the melting point, T_m, and ΔC_p is the excess of the molal heat capacity of the liquid over that of the solid. We shall use the recent values obtained in this Laboratory by the junior author,[2] *i. e.*, ΔH = 4600 cal. and ΔC_p = 5.7 cal. per degree. The melting point is 144.5°. The curve in Fig. 2 marked "ideal" has been obtained in this way.

To apply equation 1 we must know also the molal volumes of both components in the liquid form; the equation neglects any change of volume that may occur on mixing. The values for stannic iodide are extrapolated from the observations of Dorfman[5] obtained in the range, 144.5 to 275°.

For silicon chloride we use the equation of Pierre,[6] $v/v_0 = 1 + 0.001294t + 0.0_5 2184t^2 + 0.0_7 4086t^3$, obtained over the range −32 to +59°. This gives values differing appreciably from those of Thorpe, but agrees excellently with a single value reported by Mendelejeff[7] at 99.9°. Our

Table II

Values of the Parameter D^2 in Equation 1

t	$-\log N_2$	$-\log N_2^i$	V_1, cc.	V_2, cc.	ϑ_1		D^2
0	2.810	1.142	111.5	148.3	0.998		14.20
25.0	2.414	0.886	115.4	151.1	.995		13.98
40.0	2.208	.747	117.2	153.0	.992		13.78
81.3	1.628	.413	127.4	157.6	.970		13.27
88.0	1.536	.362	129.4	158.8	.964		13.13
12.1	1.191	.203	137.2	161.6	.925		12.60
115.6	1.131	.175	138.6	162.0	.917		12.50
131.0	0.185	.079	145.0	163.7	.313		12.16
		$-\log N_2'$				ϑ'	
132.0	0.642	0.256	145.4	163.8	.750	0.416	11.20
							11.95
136.0	.577	.292	147.2	164.2	.713	.463	11.05
							10.80
139.9	.409	.409	149.0	164.7	.586	.586	10.55

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[4] J. H. Hildebrand, "Solubility," Chem. Catalog Co., New York, 1936, p. 66 ff.

[5] M. E. Dorfman and J. H. Hildebrand, This Journal, **49**, 729 (1927).

[6] Pierre, *Ann. chim. phys.*, **15**, 325 (1845).

[7] D. I. Mendelejeff, *Compt. rend.*, **51**, 97 (1860).

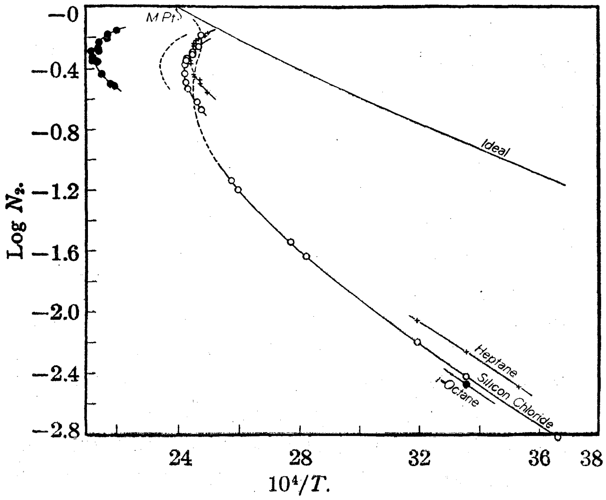

Fig. 2.—Solubility of stannic iodide.

higher temperatures involve, unfortunately, an extrapolation of this formula, but since other errors involved in the use of equation 1 cannot be avoided until a great deal more is known about the system we must be content with the following approximate analysis which, nevertheless, permits significant conclusions to be drawn.

Table II contains the values of N_2, N_2^i, V_1, V_2 and ϑ_1 used in calculating D^2, given in the last column, from equation 1.

The values for the liquid–liquid system are calculated by putting $a_2 = a_2'$ and $a_1 = a_1'$, where the unprimed letters denote the activity in one saturated liquid phase and the primed letters in the other. Writing equation 1 for both liquid phases and for both components (interchanging subscripts) yields the equation

$$RT \ln (N_2'/N_2) = V_2(\vartheta_1^2 - \vartheta_1'^2)D^2 \qquad (3)$$

and its symmetrical counterpart. This equation becomes indeterminate at the critical solution temperature, where we must use the equation[4] (p. 144)

$$RT_c(N_1V_1 + N_2V_2) = 2V_1V_2\vartheta_1\vartheta_2D^2$$

The values of D^2 so calculated are plotted against temperature in Fig. 3. It is evident that the gradual drop in D^2 becomes suddenly accentuated in the immediate neighborhood of the critical point, so that this accentuation may be regarded as a measure of the failure of equation 1 to take into account the clustering which, according to all theoretical and experimental criteria that we possess,[8] appears rather sharply in the neighborhood of the critical point, and falls off rapidly on departing therefrom either in temperature or composition. If the rate of drop of D^2 found for the solid curve were continued right up to the critical point, we would get about 11.9 instead of 10.6, and if we reversed the calculation, using 11.9 to calculate the critical temperature, we would miss it by the amount shown by the dotted curve in Fig. 2.

Although it will be desirable to make a study of the effect of volume changes and structure in the critical region before attempting a more rigid analysis, the above figures serve to show fairly well the inaccuracy caused by neglect of clustering in this region. We hope to carry out an X-ray determination of the structure of these solutions; meanwhile the attention of students of the problem by the methods of statistical mechanics is invited to this system.

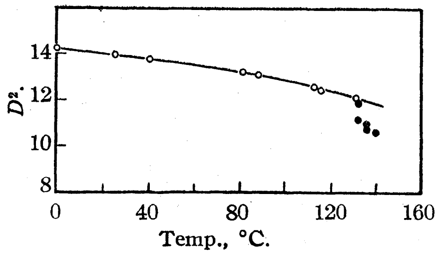

Fig. 3.—Effect of temperature on deviations for stannic iodide solutions in silicon chloride: ○, solid, ●, liquid.

Summary

Solubilities in the system silicon chloride–stannic iodide have been determined from 0 to 140°, including the range of both solid and liquid stannic iodide up to the critical solution temperatures.

This system is "regular" and free from effects of unsymmetrical molecular fields, hence is exceptionally well suited to estimate the effect of clustering in the critical region in causing deviations from the equations for regular solutions which have been derived with neglect of this effect. The error involved is about 10% in the absolute critical temperature.

BERKELEY, CALIF. RECEIVED DECEMBER 9, 1936

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[8] (a) M. v. Schmoluchowski, *Ann. Physik*, [4] **25,** 205 (1908); (b) A. Einstein, *ibid.*, **33,** 1275 (1910); (c) Wo. Ostwald, *ibid.*, **36,** 848 (1911); (d) Krishnan, *Proc. Indian Acad. Sci.*, **1,** 211, 915 (1934); **2,** 221 (1935); (e) R. Gans, *Physik. Z.*, **37,** 12 (1936); V. S. Vrklijan, *ibid.*, **37,** 482 (1936); (f) G. Scatchard and W. J. Hamer, THIS JOURNAL, **57,** 1805 (1935); (g) J. H. Hildebrand, ref. 4, p. 65.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Effect of Departure from Spherical Shape on the Viscosity Caused by Colloidal Particles and Large Molecules[1]

BY JAMES W. MCBAIN AND M. E. LAING MCBAIN

The object of the following note is to point out that accepted hydrodynamic theory applicable to colloidal particles and macromolecules does not predict a very great increase in viscosity caused by extreme departure from spherical shape. Einstein[2] is responsible for the formulas commonly employed for Brownian motion, viscosity, and diffusion of colloidal particles. He obtained these by applying the ordinary formulas for hydrodynamics, assuming that the particles were spherical and large as compared with a molecule of water, that they were uncharged, that there was no slip between them and the water with which they were actually in contact (that is, the water adhered to their surface), and, finally, that turbulence was avoided. He did not hesitate to apply his calculations to molecules of sucrose in water, relating the viscosity and diffusion with the Avogadro number which he thus deduced as being equal to 6.56×10^{23}. By this procedure he obtained the well-known formula for relative viscosity $\eta_r = 1 + 2.5v$, where the viscosity, η_r, is referred to that of the solvent, $\eta_0 = 1$, and where v is the fraction of the total volume occupied by the dispersed phase.

Notoriously, the viscosity of many dilute colloidal sols is enormously greater than that so predicted by Einstein; for example, a 0.1% solution of nitrocotton may have[3] a relative viscosity equal to 1.500, that is, an increase above the solvent equal to 0.500. This increase is many hundred times greater than the value between 0.001 and 0.002 predicted from the Einstein theory for spheres (nitrocotton being much denser than acetone).

Four explanations have from time to time been put forward. First, hydration has been postulated to raise the volume to the required value. At the present time few would care to suggest solvation (additional to, or differing from, Einstein's adherent water, but not including enclosed or enmeshed solvent) to an amount greater than one weight of solvent to one of particle. Hence this explanation can account for only one or two per cent. of the observed excess. Second, the electro-viscous effect of Smoluchowski[4] is here negligible. Third, the structural viscosity advocated by many authors[5] as the method of producing the highest apparent viscosity with the least amount of material is universally accepted for many colloids such as soap. The reasoning and data to be presented indicate that here also it is the chief operative factor.

It will be noted that according to the Einstein formula mere aggregation of molecules or colloidal particles to form larger compact massive particles or micelles has no effect upon the viscosity. To produce an effect it is necessary that the aggregation should be loose and ramifying, the molecules or particles tending to stick at points where they touch, forming an incipient "brush-heap" structure such as is now ascribed to jellies, enclosing and enmeshing tracts of free solvent.

Finally, as a result of his extensive and important work upon long chain polymers or macromolecules, Staudinger has suggested that in certain cases, such as cellulose and its derivatives, as in the case here cited, enhanced viscosity may be ascribed to the extreme elongation of the molecule. In a 0.1% solution the molecules are regarded as completely independent, although of course structural viscosity is recognized in much more concentrated solutions.

Since this hypothesis did not appear to be accessible to direct experiment, the coefficient relating viscosity to molecular elongation was obtained by empirical extrapolation from substances of lower measurable molecular weight. It has been overlooked that this calculation and extrapolation must include any tendency toward association or agglomeration, a tendency which, as is most strikingly shown in the homologous series of the soaps and the sulfonates, rapidly increases with increase in molecular weight.

This note points out the maximum possible effect that can be ascribed to elongation in increas-

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[1] Read at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] A. Einstein, *Ann. phys.*, [4] **19**, 289 (1906); **34**, 591 (1911); *Z. Elektrochem.*, **14**, 235 (1908).

[3] J. W. McBain and D. A. Scott, *Ind. Eng. Chem.*, **28**, 470 (1936).

[4] Smoluchowski, *Kolloid-Z.*, **18**, 190 (1916).

[5] For example, J. W. McBain, *J. Phys. Chem.*, **30**, 239 (1926).

ing frictional resistance to movement even when the molecule remains rigidly straight. The most extreme case so far suggested has been a long chain of glucose residues of "molecular weight" about 500,000 and with length about 5000 times the mean radius. For all other cases the effect must be less. The effect must be exhibited equally in all kinds of movement of the particles where turbulence is avoided.

The hydrodynamic formulas have been discussed by Overbeck, Lamb and Allen,[6] and are developed by Gans[7] in approximate form as follows.

The resistance to movement of a sphere is $W = 6\pi\eta\, av$. A very elongated ellipsoid is a fair model of a macromolecule or rod. For an ellipsoid of revolution, where the long semi-axis is a, the same as that of the sphere, and the other two very much smaller semi-axes, b and c, are equal, the resistance to movement is then δ times less. For the rod moving lengthwise, as when it falls in a vertical position, $\delta_a = \frac{3}{4}\left(2 \log_e \frac{2a}{c} - 1\right)$. For the rod moving broadside on, as when a horizontal fiber falls

$$\delta_c = \frac{3}{8}\left(2 \log_e \frac{2a}{c} + 1\right)$$

The terminal velocity of a falling sphere (Lamb[6]) is $\frac{2}{9} \times \frac{a^2g(s - s')}{\eta_0}$, and that of the ellipsoid $\frac{2}{9} + \frac{c^2g(s - s')}{\eta_0} \cdot \delta$, where g is the gravitational constant, $s - s'$ the difference in the density of the falling particle and the liquid, and η_0 is the viscosity of the latter. It is now easy to show that for a sphere and an ellipsoid of the same volume the ratio of their velocities is $\left(\frac{a}{c}\right)^{2/3} \times \frac{1}{\delta}$ where δ however still refers to the sphere whose diameter is equal to the length of the ellipsoid. The ratio of the two resistances to movement has this same value.

Therefore for the extreme example where $c/a = 1/2500$, and δ_a equals 12.03 and $\delta_c = 6.76$, a sphere of given weight will fall 15.3 times faster than the ellipsoid falling end on, and 27.2 times faster than the ellipsoid falling sidewise, with the intermediate positions having intermediate values. There will be no rotation of the ellipsoid as it falls,[6,7] and its deflection from the vertical fall cannot exceed 19°28′ as a maximum.[8]

Taking an average effect, for this extreme case, the frictional resistance will be only about 21-fold that of the sphere, whereas for 0.1% nitrocotton we have to explain an increase in specific viscosity of between 250- and 500-fold.

For $a/c = 100$, $\delta_a = 7.197$ and $\delta_c = 4.349$, and the sphere falls only 2.99 and 4.95 times faster than the elongated ellipsoid. For $a/c = 10$, $\delta_a = 3.744$, and $\delta_c = 2.622$, and the sphere falls 1.24 and 1.77 times faster than the elongated ellipsoid.

Hence Staudinger is correct in pointing out an influence of extreme elongation, but it is a very minor effect in comparison with viscosity increments observed. We therefore conclude that 94% or more of the total observed excess viscosity has a structural basis, whose influence is of a higher order of magnitude than that of any of the other three suggested factors.[9]

Since Lamb[6] pointed out that for purely viscous movement to be maintained, the quantity vas/η must be small compared to unity, he stated that for a silica sphere falling in water the diameter has to be small compared to 0.114 mm. Hence Stokes' law and these relations apply only to much smaller particles, which are not readily subjected to experimental study. We have attempted to overcome this difficulty by employing instead of water 60% sucrose solution, whose viscosity is 56.2-fold greater at 20°.

Our procedure was to let thin silica fibers fall through water and the sucrose solution in a vertical and in a horizontal position and also in intermediate positions. Afterward the same fibers were fused into spherical form and then time of fall was again observed. The fibers fell in water always without change in orientation, but usually failed to do so in the sucrose solution. Likewise the difference in rate between fiber and sphere was less than that calculated. Part of this was found to be due to volatilization of the silica during fusion. Also each "sphere" had a thickened tail which could not be completely removed. Hence the spheres were compared with fibers of the same

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(6) A. Overbeck, *Crelle*, **81**, 62 (1876); H. Lamb, "Hydrodynamics," Cambridge University Press, 1906, p. 554; H. S. Allen, *Phil. Mag.*, [5] **50**, 323, 519 (1900).

(7) R. Gans, *Sitzb. math. physik. Klasse Akad. München*, 191 (1911); *cf.* Guy Barr, "A Monograph of Viscometry," Oxford University Press, London 1931, p. 195.

(8) For recent discussions of the hydrodynamic equations where rotation is involved and experiments in which orientation and interference between rod-like particles (structural viscosity) occur, see for example Guth, *Kolloid-Z.*, **75**, 15 (1936); Eirich, Margaretha and Bunzl, *ibid.*, 20 (1936). See also Gans, *Ann. Phys.*, [4] **86**, 652 (1928); and Jeffrey, *Proc. Roy. Soc.* (London), **A102**, 176 (1923).

(9) In a private communication Dr. S. S. Kistler adds the information, confirmatory of the present conclusion, that owing to the difference in behavior of a sphere and of a cylinder (Lamb, *Phil. Mag.*, **21**, 112 (1911)) with regard to very low Reynolds numbers, the force acting upon a cylinder of the same volume as a sphere will not be much larger than that on the sphere.

weight, 59.7 mm. long where the ratio of length to diameter was only 1933 instead of 2500. The diameter of the fibers was 0.040 mm., that of the spheres 0.485 mm.; probably they were all still too coarse for the requirements of the formula, but the results are of interest as approximately illustrative of the general formulas.

Vertical fibers fell 17.7 cm. through sucrose solution in 901 and 949 seconds, respectively, whereas the spheres required a minimum of 84 sec. The value calculated for the sphere from Stokes' formula was 68.9 sec. The ratio between the fibers and the theoretical value for the sphere was 13.07 and 13.77, mean 13.4, whereas the theoretical ratio predicted was 13.3, and the actual ratio found was not larger than 11. In water, typical experiments gave a ratio between that observed for a vertical fiber and that calculated for a sphere the same weight equal to 14.3 as compared with the predicted value 15.3.

The effect of elongation is even less under conditions where turbulence is prominent in the observation of rate of fall. For the silica fibers and spheres falling through water the observed effect was only between 4-fold for vertical and 8-fold for horizontal fall. In dropping $^3/_8''$ (9.5 mm.) steel balls through still water and comparing them with the same weight of steel wire (0.0243″ (0.61 mm.) in diameter) whose length was again 5000 times its radius, the relative rates varied only between 1.6 for vertical and 4.5 for horizontal. Hence, in viscosity measurements the effect of elongation is even less when turbulence is not eliminated.

Summary

From observations on the actual effect on resistance to movement when a sphere is elongated to a fiber 2500 longer than its diameter, it is concluded in accordance with the hydrodynamic theory employed by Einstein for colloidal particles and large molecules that although the effect of extreme departure from sphericity is measurable it is of too low a magnitude to explain the high viscosity which 0.1% of certain colloids, such as nitrocotton, impart to solvents in which they are dissolved. It is therefore concluded that the chief factor is structural viscosity due to entanglement and local adherence of molecules and particles, effectively immobilizing a disproportionate amount of the solvent in comparison with the amount of the colloid itself.

STANFORD UNIVERSITY, CALIF.

RECEIVED NOVEMBER 25, 1936

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

An X-Ray Study of Some Linear Polyesters

BY C. S. FULLER AND C. L. ERICKSON

By means of intermolecular polycondensation reactions Carothers and his co-workers[1] have been able to synthesize linear polyesters of high molecular weight from dihydric alcohols and dibasic aliphatic acids. Carothers and Hill[2] have pointed out the surprising fiber-like characteristics which can be obtained in certain of these polyesters when the molecular weights are sufficiently high (superpolyesters). They have also demonstrated that the polyesters in massive form are microcrystalline, furnishing sharp X-ray powder diagrams, while in the oriented state (cold-drawn fibers) they are capable of giving fiber patterns. Up to this time, however, no attempt apparently has been made to verify the chemical structures which have been proposed for these compounds by means of a study of their X-ray fiber patterns.[3] The X-ray structure of synthetic fibers of known chemical constitution is also of considerable interest since it offers a means of confirming present conceptions in regard to high polymeric substances.

In the present investigation a series of polyesters has been prepared and examined by means of X-rays. Six of these have been carried to the superpolyester state so that highly oriented fiber patterns could be obtained from them. It is the purpose of this investigation to present and discuss the results of the measurement of these fiber patterns.

Materials and Method

Since many polyesters do not crystallize, or do so very slowly, the number which is suitable for X-ray study is somewhat limited. Table I lists the materials which have been investigated together with the approximate molecular

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(1) W. H. Carothers, THIS JOURNAL, **51**, 2548 (1929), *et seq.*

(2) W. H. Carothers and J. W. Hill, *ibid.*, **54**, 1579 (1932).

(3) A. W. Kenney (ref. 2) has found that the fiber period of some polyesters approximates the length of the chemical repeating unit.

weights,[4] the melting[5] or softening points, densities and drawing properties of each. The preparation and other properties of these materials are described in the experimental part of this paper.

For the purpose of obtaining the X-ray diagrams the substances were examined in the form of bars (for the Debye–Scherrer photographs) 0.4 mm. thick, 1.0 mm. wide and about 15 mm. long or in the form of cylindrical fiber bundles (for the fiber diagrams) 0.5 to 1.0 mm. in diameter. The fibers were prepared by cooling the molten polyesters into solid rods of suitable sizes and cold drawing these so as to form well oriented fibers. These were then wound under tension on U-shaped holders so as to form bundles of parallel fibers. The fiber bundles were fixed in a perpendicular position to the X-ray beam which was collimated to a diameter approximately equal to that of the sample.

The X-ray cameras employed were similar in construction to those described by J. R. Katz.[6] Except in the case of very weak or diffuse reflections the precision of measurement of the X-ray reflections was approximately 1% on check photographs of the same material.

The source of X-rays was a Philips Metalix X-ray tube which was operated at 13 ma. and approximately 25 kv. A copper target was employed and the resulting K-alpha radiation (1.539 Å.) separated from the K-beta by means of a nickel filter 0.015 mm. thick. The maximum due to the white radiation, which occurred at approximately 0.8 Å., was observed near the primary beam in nearly all cases but it is not believed that the effects due to it have been confused with the monochromatic reflections from the samples. Exposure times varied between four and six hours.

Results

Debye–Scherrer photographs of samples of polyethylene sebacate representing bands of progressively increasing average molecular weight (1–4, Table I) showed the same interplanar spacings within the precision of measurement in all cases. The relative intensity (visual) of corresponding rings was also found to be the same on all photographs. The interplanar distances determined from these photographs agreed with those determined from the fiber pattern of polysebacate.

Highly oriented fiber diagrams were obtained from polyethylene succinate, polyethylene adipate, polyethylene azelate and polyethylene sebacate. The fibers drawn from polytrimethylene sebacate and polydiethyleneoxide sebacate yielded less well defined photographs. In all cases an uniaxial type of crystallite orientation is present. Several attempts to produce a higher degree of orientation[7] (folienstruktur) by rolling the polyethylene sebacate ester into thin films showed that no further orientation of the crystallites occurred, since the same fiber diagram was obtained when the film was exposed parallel and perpendicular to the film plane. Further efforts to secure such samples of higher orientation are being made. In Fig. 1, (a) to (f) are schematic drawings of the fiber patterns obtained from the six polyesters.

TABLE I

PROPERTIES OF THE POLYESTERS

		Average mol. wt.	Softening point, °C.	Density (25°C.)	Cold-drawing properties
		Debye–Scherrer photographs			
1	P-ethylene sebacate	4,000	69	. . .	Does not draw
2	P-ethylene sebacate	13,000	69–70	. . .	Does not draw
3	P-ethylene sebacate	15,000	68–71	. . .	Draws well
4	P-ethylene sebacate	18,000	70–74	1.148	Draws well
		Fiber patterns			
5	P-ethylene succinate	13,000	104–106	1.358	Draws well
6	P-ethylene adipate	12,000	52–54	1.250	Draws well
7	P-ethylene azelate	10,000	44–46	1.172	Draws well
8	P-ethylene sebacate (same as 4)	18,000	70–74	1.148	Draws well
9	P-trimethylene sebacate	13,000	54–55	1.090	Draws well (cold)
10	P-diethylene oxide sebacate	18,000	36.5–39	1.128	Draws well (cold)

In the case of each of the polyesters the identity periods along the fiber axis have been calculated from averaged measurements of the reflections obtained from at least two and generally three independent exposures. The interplanar distances, identity periods along the fiber axes and relative intensities of the reflections for the six polyesters listed in Table I, 5–10 are recorded in Table II. The average values of the fiber periods are collected in the second column of Table IV. In the case of polyethylene azelate, polytrimethylene sebacate and polydiethyleneoxide sebacate several values for the fiber periods are possible because of

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(4) No great significance can be attached to the molecular weight values in Table I since in every case mixtures of polymers are present. The values here given were obtained by the use of Staudinger's viscosity method ("Die hochmolekulären organischen Verbindungen"). The constant ($y = 1.5 \times 10^{-3}$) given by Staudinger and Schwalenstöcker (ref. 20) for aliphatic glycol esters in chloroform solution has been employed.

(5) As W. H. Carothers and J. A. Arvin, THIS JOURNAL, **51**, 2560 (1929), have pointed out the melting points are not sharp.

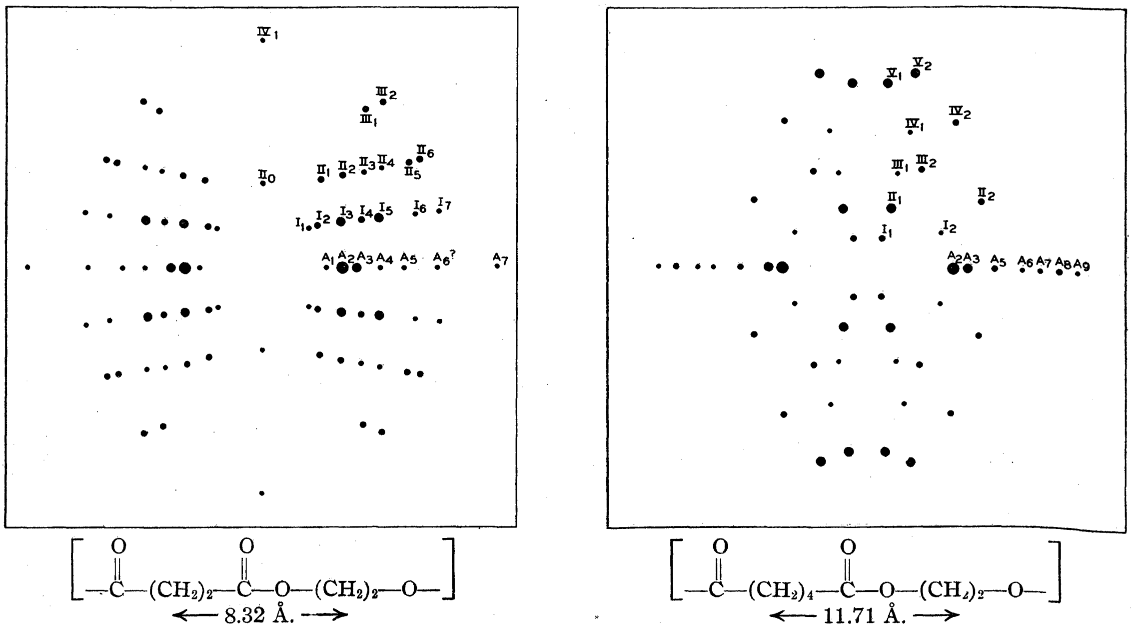
(6) J. R. Katz, "Die Roentgenspektrographie als Untersuchungsmethode," Urban and Schwarzenberg, Berlin, 1934, p. 54.

(7) K. Weissenberg, *Ann. Physik*, **69**, 409 (1922); W. A. Sisson, *J. Phys. Chem.*, **40**, 343 (1936).

missing spectra. A consideration of the chemical structures, however, together with the probable lengths of the radicals involved, leads in each case to a choice of the value given as the true one.

For polyethylene azelate it appears from these considerations that only every third layer-line is present up to the sixth layer-line. In the case of polytrimethylene sebacate the first six layer-lines prove to be missing and in the case of polydiethyleneoxide sebacate the layer-lines 1, 2, 3, 5, 6, 7 are absent or very weak.

Strong diatropic planes occur in the normal fiber diagram for polyethylene azelate (Fig. 1 (c)), indicating the presence of a two-fold screw axis of symmetry parallel to the fiber axis. Polytrimethylene sebacate and polydiethyleneoxide se-

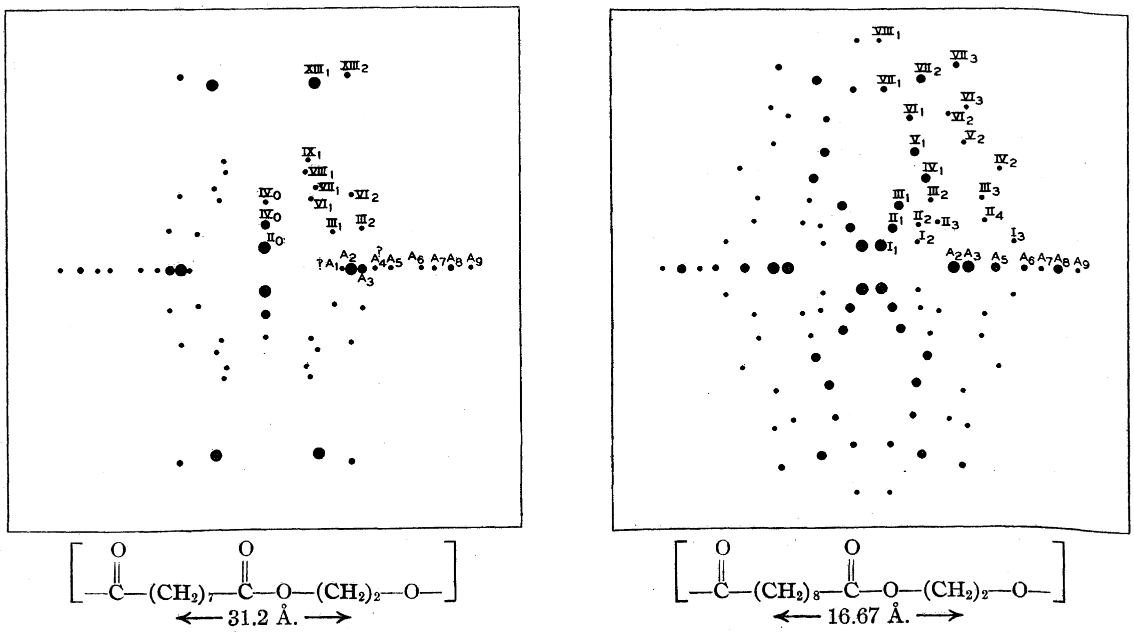


$[-\overset{\text{O}}{\overset{\|}{\text{C}}}-(\text{CH}_2)_2-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-(\text{CH}_2)_2-\text{O}-]$ ← 8.32 Å. →

(a) Polyethylene succinate.

$[-\overset{\text{O}}{\overset{\|}{\text{C}}}-(\text{CH}_2)_4-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-(\text{CH}_2)_2-\text{O}-]$ ← 11.71 Å. →

(b) Polyethylene adipate.



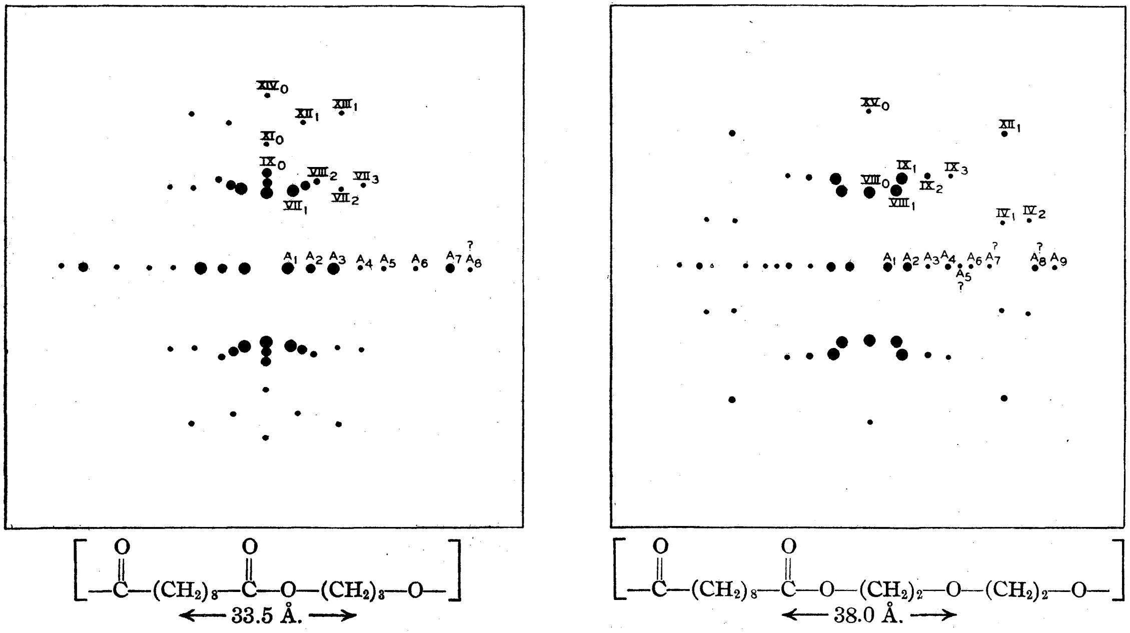
$[-\overset{\text{O}}{\overset{\|}{\text{C}}}-(\text{CH}_2)_7-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-(\text{CH}_2)_2-\text{O}-]$ ← 31.2 Å. →

(c) Polyethylene azelate.

$[-\overset{\text{O}}{\overset{\|}{\text{C}}}-(\text{CH}_2)_8-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-(\text{CH}_2)_2-\text{O}-]$ ← 16.67 Å. →

(d) Polyethylene sebacate.

Fig. 1.—Schematic drawings of the fiber diagrams of the polyesters.



$$\left[-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_8-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_3-O-\right]$$

$\longleftarrow$ 33.5 Å. $\longrightarrow$

$$\left[-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_8-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_2-O-(CH_2)_2-O-\right]$$

$\longleftarrow$ 38.0 Å. $\longrightarrow$

(e) Polytrimethylene sebacate.

(f) Polydiethyleneoxide sebacate.

Fig. 1.—Schematic drawings of the fiber diagrams of the polyesters.

bacate also show strong reflections on the meridian line which appear to arise from planes parallel to (001). Diatropic planes for the other esters were sought by exposures in which the primary beam formed various acute angles with the fiber axes (Schiefeaufnahme). In this way a definite diatropic plane was found on the second layer-line of the polyethylene succinate diagram indicating the presence of a two-fold screw axis. No strong diatropic planes were observed for polyethylene sebacate or polyethylene adipate. However, weak reflections appear to exist on the seventh and fifth layer-lines of these esters, respectively. Calculations of the fiber periods from the diatropic planes agree well with those made in the usual manner by the application of the Polanyi equation.[8]

The limitations of the fiber diagram in furnishing further crystallographic information other than the identity period along the fiber axis have often been pointed out.[9] There are, however, certain observations which can be made on these diagrams which are of value, especially when chemically related substances of known constitution are under consideration. In addition, in cases where the diagrams are rich in reflections and in which the reflections are sharp enough to allow accurate measurements of the spacings to be obtained, the method, based on the use of the reciprocal lattice, described by Sauter,[10] offers a means of indexing the reflections and arriving at a plausible determination of the unit cell. These solutions are, of course, not necessarily unique[11] but they serve the purpose of furnishing a basis for further crystallographic study.

This method has been applied to each of the fiber diagrams represented in Fig. 1 (a) – (f) with the results summarized in Table III.

A comparison of the fiber diagrams of the six polyesters (Fig. 1) shows immediately that the crystal structure of polyethylene adipate, azelate and sebacate are very similar to one another and different from the other esters. For example, the equatorial spacings prove to be almost identical within the limit of experimental error and the arrangement and intensity of the layer-line reflections is analogous in all three cases.[12] There can be little doubt therefore that these esters possess

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(8) M. Polanyi, *Z. Physik*, **7**, 149 (1921).

(9) J. R. Katz, *Trans. Faraday Soc.*, **32**, 77 (1936); H. Mark, "Physik und Chemie der Cellulose," Julius Springer, Berlin, 1932, p. 136; Trogus and Hess, "Ergeb. der tech. Roentgenkunde," Vol. IV, Eggert and Schiebolt, Akademische Verlagsgesellschaft, Leipzig, 1934, p. 60.

(10) E. Sauter, *Z. Krist.*, **84**, 453 (1933).

(11) For example the reflections of the ethylene adipate, azelate and sebacate esters in Table II agree almost as well, with orthorhombic units cells of cross-section: a = 21.8 Å., b = 33.3 Å., and c-axes equal to the corresponding fiber periods as with the monoclinic cells proposed in Table III.

(12) Two additional weak equatorial reflections occur in the case of the azelate. These, however, may be due to errors in observation or to planes too weakly reflecting to be observed in the other esters.

TABLE II

INTERPLANAR DISTANCES AND FIBER PERIODS OF POLYESTERS

Reflection	P-ethylene succinate			P-ethylene adipate			P-ethylene azelate			P-ethylene sebacate			P-trimethylene sebacate			P-diethyleneoxide sebacate		
	d, Å.	I	Int.	d, Å.	I	Int.	d, Å.	I	Int.	d, Å.	I	Int.	d, Å.	I	Int.	d, Å.	I	Int.
A_1	5.37		V W	..?		..	4.63?		V W	..?		..	15.6		V S	17.7		V S
A_2	4.41		V S	4.15		V S	4.17		V S	4.17		V S	7.82		S	8.87		S
A_3	3.85		S	3.63		S	3.70		S	3.67		V S	5.22		V S	5.90		W
A_4	3.12		W	..?		V W	3.30?		W	3.42?		V W	3.86		V W	4.39		M
A_5	2.70		V W	2.95		M	2.97		M	2.96		S	3.14		W	3.88?[a]		W
A_6	2.29?		V W	2.52		W	2.49		W	2.51		M	2.56		V W	3.50		W
A_7	1.92		W	2.36		V W	2.36		V W	2.36		V W	2.21		S	2.69?[a]		W
A_8				2.17		M	2.21		M	2.18		S	2.10?		W	2.36?[a]		M
A_9				2.08		W	2.08		W	2.08		W				2.19		W
I_1	5.68	8.87	W	10.3	11.22	M				14.7	16.51	V S						
I_2	5.02	8.56	M	5.35	11.34	W				6.64	16.14	W						
I_3	3.91	8.36	S							2.63	(21.69)	V W						
I_4	3.31	8.39	M															
I_5	2.94	8.13	S															
I_6	2.43	7.99	V W															
I_7	2.19	7.90	V W															
II_0	4.17	8.34	W				15.8	31.6	V S									
II_1	3.46	8.36	M	5.46	11.78	S				7.57	16.71	S						
II_2	3.04	8.33	M	2.88	11.77	M				5.35	16.84	W						
II_3	2.73	8.27	W							4.39	16.00	W						
II_4	2.52	8.19	W							3.00	16.71	V W						
II_5	2.26	8.29	M															
II_6	2.18	8.31	M															
III_1	2.20	8.47	M	3.67	11.85	W	4.51	29.8	W	5.14	16.92	S						
III_2	2.09	8.30	M	3.31	11.70	M	3.39	(27.9)	W	3.97	16.39	W						
III_3										2.88	16.89	W						
IV_0							7.78	31.1	S									
IV_1	1.98	..	W	2.72	11.85	W				3.47	16.83	S				2.69	(36.0)	V W
IV_2				2.37	11.80	M				2.43	16.76	V W				2.36	37.8	V W
V_1				2.23	12.01	S				3.02	16.72	S						
V_2				2.12	11.78	S				2.52	16.84	W						
VI_0							5.18	31.1	W									
VI_1							4.26	31.6	W	2.56	16.76	M						
VI_2							3.24	31.2	W	2.35	16.74	W						
VI_3										2.21	16.71	W						
VII_0													4.77	33.4	V S			
VII_1							3.75	31.7	V W	2.30	...	M	4.28	31.9	V S			
VII_2										2.16	16.81	S	3.38	33.3	W			
VII_3										2.01	16.77	M	2.97	32.5	W			
VII_4										1.89	...	W						
VIII_0													4.19	33.5	S	4.80	38.4	V S
VIII_1							3.46	30.9	W	1.97	...	M	3.91	34.8	S	4.43	38.0	V S
VIII_2													3.63	33.3	M			
IX_0													3.78	34.0	S			
IX_1							3.17	31.5	W							3.83	37.0	V S
IX_2																3.40	37.8	M
IX_3																3.04	37.0	W
XI_0													3.04	33.4	W			
XII_1													2.58	33.7	W	2.17	39.1	M
XIII_1							2.18	31.4	V S				2.31	35.6	V W			
XIII_2							2.12	31.3	M									
XIV_0													2.36	33.0	W			
XV_0																2.58	38.7	W

[a] These reflections are probably pseudo-equatorial points formed by the overlapping of layer-line arcs.

unit cells of the same dimensions in the plane at right angles to the fiber axis and belong to the same crystal system. That this is the case is confirmed by a calculation of the number of chain molecules (number of X-ray repeating units) passing through the unit cell in each case from the formula

$$Z = Vd/1.65\,M \qquad (1)$$

where V, d and M are the volume of the unit cell, the density (Table I) and the molecular weight of the repeating unit, respectively. The values of Z

TABLE III

MINIMUM VALUES FOR THE UNIT CELLS OF THE POLYESTERS

	a	b	c[1]	β	z
P-ethylene succinate	9.05	11.09	8.32	102.8	4.6
P-ethylene adipate	25.7	30.7	11.71	103.8	39.5
P-ethylene azelate	25.7	30.7	31.2	103.8	39.8
P-ethylene sebacate	25.7	30.7	16.67	103.8	39.0
P-trimethylene sebacate	31.2	31.2	33.5	90	44.5
P-diethylene oxide sebacate	17.6	17.6	38.0	90	14.8

[1] Fiber period.

are given in Table III and for the esters in question are identical within the limit of error.

There is likewise a close similarity between the fiber diagrams obtained for polytrimethylene sebacate and polydiethyleneoxide sebacate. In these cases, although the equatorial spacings are not identical, the fact that one side spacing, different in each case, occurs in several orders makes a tetragonal form of unit cell probable.

Discussion

Crystal Lattice of the Polyesters.—Carothers[13] has suggested that the linear polyesters may have a macromolecular type of crystal lattice[14] in which molecules of various lengths crystallize together. Since the reflections corresponding to the lengths of even the smallest polymers of these compounds would fall very close to the central beam, the identity of the Debye–Scherrer photographs (1–4, Table I) does not constitute proof that such a lattice does or does not exist.[15] In whatever manner in which the individual molecules are grouped in the crystal lattice, however, the existence of well-defined fiber diagrams shows that the microcrystals are arranged with an important crystallographic axis parallel to the direction of the fiber axis and that all degrees of rotation around this axis exist. Furthermore, the observation of meridian reflections (from planes perpendicular to the fiber axis) requires the presence of crystal systems of symmetry higher than the triclinic and also that the orthogonal monoclinic axis is parallel to the fiber axis. The molecules in the polyesters therefore should be arranged in the crystals with their long axes parallel to the fiber direction.

The determination of the exact arrangement of the long chain molecules in the unit cells with regard to axial orientation and displacement lengthwise relative to one another is much too complex a problem to be solved on the basis of the existing data. The relatively large number of chains involved in the unit cells suggests that the positions with respect to one another are determined by the interaction of the polar carbonyl groups along the chains in such a way that identity is established only after the association of a considerable number of chains. It should be emphasized again that the unit cells which have been given above as a result of the application of the reciprocal lattice method are not necessarily the true ones since they are based on the data provided by fiber patterns alone. It is believed, however, that the lengths of the axes found for these cells as given in Table III at least set a lower limit to the size since it is not possible to secure satisfactory agreement with the observed reflections if smaller values are assumed.

Chain Configurations of the Polyesters.—Lycan and Adams[16] and Carothers and Arvin[5] have postulated a long chain structure for the polyesters. As in the case of most reactions leading to high polymers, chain molecules of various lengths are formed.[17] The X-ray studies of Müller[18] and others on the paraffins and aliphatic acids have established the fact that planar zig-zag chains of carbon atoms joined at the tetrahedral angle are present. The recent work of Sutton and Brockway[19] has shown that the tetrahedral angle is observed (within a few degrees) for oxygen in ethereal linkage. These authors have also determined accurately the length of the C–O bond as 1.43 Å. These data, together with the known C–C bond distance of 1.54 Å., enable the calculation of the lengths of the chemical repeating units of the polyesters on the assumption that planar zig-zag chains are present.

The results of these calculations are given in the third column of Table IV. The fourth column of this table records the difference between the observed and calculated periods referred to the chemical repeating unit. It is noted immediately that in the case of the esters having an odd number of chain atoms (3, 5 and 6, Table IV) the length of the chemical repeating unit is approximately one-half the observed fiber period. Since this occurs for the polyethylene azelate in which the acid is odd and in the polytrimethylene sebacate and polydiethyleneoxide sebacate in which the glycols are odd and does not occur for the even esters, the presence of a zig-zag chain is indicated. However, the difference between the observed and calculated lengths of the chemical repeating units (column 4, Table IV) is in all cases too large to be accounted for by experimental error. We must conclude, therefore, that the chains are

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[13] W. H. Carothers, *Chem. Rev.*, **8**, 416 (1931).

[14] H. Staudinger and R. Signer, *Z. Krist.*, **70**, 193, 202 (1929).

[15] *Cf.* J. Hengstenberg, *Ann. Physik*, **84**, 245 (1927); E. Sauter, *Z. physik. Chem.*, **18B**, 417 (1932); **21B**, 161, 186 (1933).

[16] W. Lycan and R. Adams, THIS JOURNAL, **51**, 625, 3450 (1929).

[17] W. H. Carothers, *Trans. Faraday Soc.*, **32**, 48 (1936); P. J. Flory, THIS JOURNAL, **58**, 1877 (1936).

[18] A. Müller, *J. Chem. Soc.*, **123**, 2043 (1923), *et seq.*

[19] L. E. Sutton and L. O. Brockway, THIS JOURNAL, **57**, 473 (1935).

either planar but not zig-zag or that they are non-planar. Since it has not been possible to obtain satisfactory agreement with the observed fiber periods on the basis of any planar arrangement of atoms, it is believed that the polyesters have non-planar chain configurations.

TABLE IV

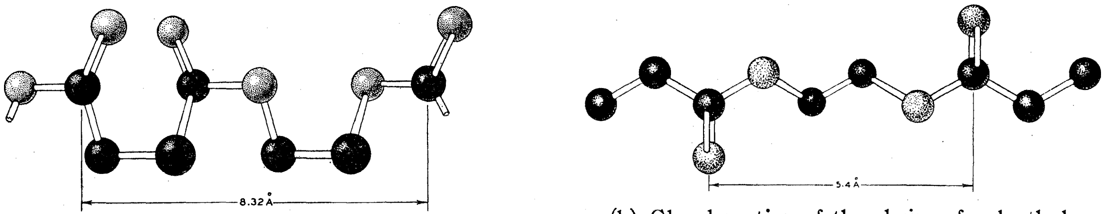
COMPARISON OF OBSERVED AND CALCULATED FIBER PERIODS (ÅNGSTRÖM UNITS)

	Polyester	Obsd. fiber period	Calcd. chem. rep. unit	Difference based on chem. rep. unit
1	P-ethylene succinate	8.32 ± 0.06	9.70	1.4
2	P-ethylene adipate	11.71 ± .07	12.21	0.5
3	P-ethylene azelate	31.2 ± .2	16.0	.4
4	P-ethylene sebacate	16.67 ± .06	17.24	.5
5	P-trimethylene sebacate	33.5 ± .3	18.5	1.7
6	P-diethyleneoxide sebacate	38.0 ± .3	20.8	1.8

This is particularly the case with polyethylene succinate, in which the observed fiber period of 8.32 Å. can be produced only by a helical arrangement of the chain atoms. The close analogy to the polymethyleneoxides and polyethyleneoxides described by Sauter[16] is particularly striking, and suggests that the spiral structure is derived from the cis or "tub" form of chain rather than from the zig-zag form. Figure 2 (a) illustrates this type of chain.

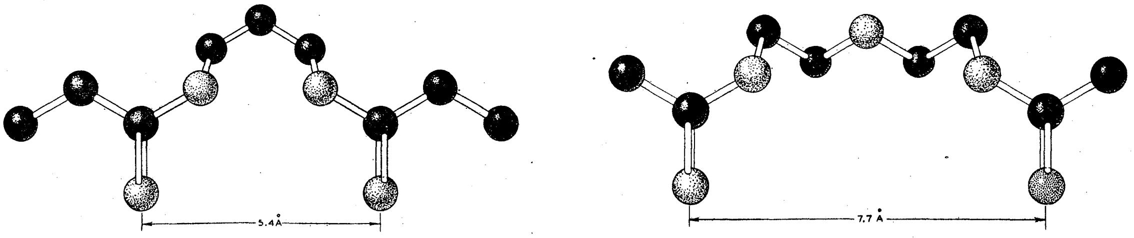
The equality of the differences observed in Table IV for the ethylene glycol esters of adipic, azelaic and sebacic acids is again in agreement with the identities in the dimensions of the unit cells mentioned above, and suggests that these esters have the same chain configuration and depart only slightly from the plane zig-zag arrangement of chain atoms. The constancy of the deviation (*ca.* 0.5 Å.) indicates that any shortening of the chains occurs in the ethylene glycol portion since the acid portions of the chains are of varying lengths. Figure 2 (b) shows how a shortening of the planar zig-zag chain may arise through a displacement of the chain oxygen atoms toward one another. This motion of the oxygen atoms results in forcing the carbon atoms between them out of the plane of the chain.

The last two esters, polytrimethylene sebacate and polydiethyleneoxide sebacate, in Table IV likewise show deviations from the planar zig-zag form. A number of configurations which agree with the observations is possible in these cases. It might be assumed that since the sebacic acid radical in polyethylene sebacate appears planar, this structure would be retained in its other esters. If this assumption is made the shortening can be accounted for in the glycol radical. Figure 2 (c) and (d) indicate (schematically) glycol configurations for these esters which produce the desired agreement.



(a) Chain atoms of polyethylene succinate.

(b) Glycol portion of the chains of polyethylene adipate, polyethylene azelate and polyethylene sebacate.



(c) Glycol portion of the chain of polytrimethylene sebacate.

(d) Glycol portion of the chain of polydiethyleneoxide sebacate.

Fig. 2.—Chain configurations of the polyesters which reproduce the observed spacings. Dark balls represent carbon and light balls represent oxygen atoms.

Staudinger and Schwalenstöcker[20] on the basis of viscosity studies report that ethylene glycol esters in solution have an extended form of chain which is shortened because of the attraction of the "secondary valences" of the oxygen atoms. Since these authors believe their conclusions apply equally well to the solid state, it might be expected that the polyesters would behave in a similar manner with regard to the glycol configuration. The chain forms given above are in qualitative agreement with the conclusions of Staudinger and Schwalenstöcker. It therefore seems reasonable to conclude that the chain configurations assumed by the polyesters can be regarded as resulting from the attractions of atoms or dipoles attached at intervals to the chains.

Experimental Part

The polyesters were prepared by heating together dibasic acids and glycols according to a modification of the method employed by Carothers and Arvin.[5] The acid and the glycol (in the ratio of 1 to 1.05 moles) corresponding to the ester desired were placed in a distilling flask deeply immersed in a sand-bath. A slow stream of pure, dry nitrogen was bubbled through the heated mixture during the reaction. The nitrogen served the purpose of providing an inert atmosphere and of removing the water formed in the reaction. For the first few hours of reaction a condenser and receiver were attached to the flask. During this time the temperature rose from about 160 to 180° and about 75 to 90% of the theoretical amount of water distilled over. The temperature was then raised to 200 ± 10° and maintained at this point until the molecular weight required for cold drawing was obtained (forty-eight to one hundred and twenty hours). The samples of polyethylene sebacate of lower average molecular weight than that required for cold drawing were obtained by taking out samples periodically during the reaction.

The succinic (m. p. 184–186°), adipic (m. p. 151–153°) and sebacic (m. p. 129–129.5°) acids were obtained from the Eastman Kodak Company. The azelaic acid (m. p. 106°) was prepared from castor oil by oxidation of the ricinoleic acid by means of potassium permanganate.[21] The glycols employed for the preparation of the esters were obtained by distilling the purest compounds that could be obtained commercially. In each case the middle portion was selected. The ethylene glycol was distilled at atmospheric pressure (b. p. 195–195.5°), the trimethylene glycol and diethyleneoxide glycol were distilled under reduced pressure.

The polyesters prepared as above showed the following values of carbon and hydrogen on ultimate analysis as compared with theoretical. Polyethylene succinate—found, 50.03% C, 5.93% H; calcd., 49.98% C, 5.59% H. Polyethylene adipate—found, 55.85% C, 6.67% H; calcd., 55.78% C, 7.03% H. Polyethylene azelate—found, 61.75% C, 8.41% H; calcd., 61.64% C, 8.47% H. Polyethylene sebacate—found, 63.71% C, 8.41% H; calcd., 63.11% C, 8.84% H. Polytrimethylene sebacate—found, 64.97% C, 8.93% H; calcd., 64.41% C, 9.16% H. Polydiethyleneoxide sebacate—found, 62.31% C, 8.83% H; calcd., 61.72% C, 8.89% H. These were considered sufficiently pure for the X-ray work. Small portions of the polyesters were purified by solution in chloroform and precipitation with petroleum ether for the determination of the densities and the softening points.

Summary

1. Debye–Scherrer photographs of polyethylene sebacates of increasing average molecular weight are identical and show the same interplanar spacings as the fiber diagrams of the oriented materials.

2. Fiber diagrams of six highly oriented polyesters show that in the oriented state the chain molecules are parallel to the axes of the fibers. A comparison of the observed fiber periods with the lengths of the chemical repeating units calculated on the basis of a planar zig-zag chain shows that polyethylene succinate possesses a helical arrangement of the chain atoms whereas polyethylene adipate, polyethylene azelate and polyethylene sebacate have similar configurations which deviate only slightly from the planar zig-zag form. The sebacate polyesters of trimethylene glycol and diethyleneoxide glycol also conform best to a configuration in which the chain atoms are nonplanar. The deviations of the configurations from the planar zig-zag type of chain are attributed to attractive forces residing in the ester groups.

3. The data obtained from the fiber patterns have been treated graphically and solutions for the unit cells found which agree in all cases with the observed interplanar spacings.

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[20] H. Staudinger and H. Schwalenstöcker, *Ber.*, **68**, 727 (1935).

[21] *Organic Syntheses*, **13**, 3 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CHICAGO]

Studies in Proteins. VI. The Solubility of the Nitrogenous Constituents of Certain Seeds in Sodium Chloride Solutions

BY L. P. O'HARA AND FELIX SAUNDERS

Introduction

These studies were undertaken principally in the hope that a more precise and explicit definition of globulins might be proposed. At present no two writers of textbooks on biochemistry define globulins in the same way. For example: Globulins are "soluble in dilute solutions of neutral salts, not soluble, however, in concentrated solutions; precipitated by half-saturated ammonium sulfate" (Williams)[1]; "simple proteins insoluble in pure water but soluble in neutral solutions of salts of strong bases with strong acids" (Bodansky)[2]; "insoluble in water, but soluble in neutral dilute solutions of salts of strong bases and acids, such as sodium chloride" (Mathews).[3] According to the "Joint Recommendation of the Physiological and Biological Committees on Protein Nomenclature"[4] globulins should be defined as "simple proteins insoluble in pure water but soluble in neutral solutions of salts of strong bases with strong acids." Gortner[5] has questioned the validity of these definitions. He says, "a definition which is based upon solubility, *i.e.*, peptization in a dilute salt solution, is so ambiguous as to be absolutely meaningless."

In the preceding papers of this series the following facts have been brought out. (1) As would be expected from the usual definitions of globulins, normal alkali halide salts extract from orange-seed meal the same amount of protein (pomelin) and nitrogenous material.[6] (2) Normal solutions of various sodium salts, some neutral and some alkaline, extract the same amount of nitrogenous material, presumably protein, from orange-seed meal.[7] The present work was undertaken in order to determine how much nitrogenous material is extracted by different concentrations of sodium chloride from various seed meals so that we may test our definition of globulins on another point, that of solubility in concentrated salt solutions.

Experimental

The seeds were ground, defatted and sifted in the manner already described.[7] The orange-seed meal was 60–80 mesh, the peanut meal and the flaxseed meal were 80–100 mesh. Total nitrogen was determined for the air-dried seed meal. A weighed amount[8] of the seed meal was placed in a 250-cc. centrifuge bottle and 50 cc. of solution added. The bottles were shaken for thirty minutes in a mechanical shaker, centrifuged for twenty minutes and the supernatant liquid decanted directly into a Kjeldahl flask. The extraction was repeated two more times and the total nitrogen determined in the combined solutions by the Kjeldahl macro method.

As long as the scope of the investigation had to be limited it seemed best to select seeds representing as many different types as possible. Consequently, the following seeds were chosen: orange and flax, which yield crystalline globulins; peanut, which gives a well-defined but non-crystalline globulin; and rye, which probably does not contain any globulin. Sodium chloride was chosen because it is the salt most commonly used in protein-extraction studies.

In order to study the effect of time a series of extractions was run on flaxseed meal with 0.37 *N* sodium chloride. The time intervals for extraction were one-half, two, and four times the usual interval. The results as shown in Table I indicate that time is a negligible factor within the limits chosen for this experiment.

TABLE I

THE EFFECT OF TIME UPON THE AMOUNT OF NITROGENOUS MATERIAL EXTRACTED FROM FLAXSEED MEAL BY 0.37 *N* SODIUM CHLORIDE

Time (x = usual time interval)	Total N extracted, %
0.5x	60.77
1.0x	60.46
2.0x	59.82
4.0x	60.68

Several times, especially during the summer months, discordant results were obtained. It was finally concluded that the deviations might be due to temperature changes which are often very marked and sudden in Chicago. In order to check this hypothesis, several extractions of seed meal with 4 *N* sodium chloride were run at various temperatures. The results (Table II) clearly show a temperature coefficient. Temperature changes are probably negligible during the winter when buildings are steam heated, but during the summer temperature must be con-

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(1) Williams, "Introduction to Biochemistry," D. Van Nostrand Company, Inc., New York, 1931.

(2) Bodansky, "Introduction to Physiological Chemistry," 3rd ed., John Wiley and Sons, Inc., New York, 1934.

(3) Mathews, "Principles of Biochemistry," William Wood and Co., Baltimore, 1936.

(4) *J. Biol. Chem.*, **4**, xlviii (1908).

(5) "Outlines of Biochemistry," John Wiley and Sons, Inc., New York, 1929.

(6) Saunders, THIS JOURNAL, **53**, 696 (1931).

(7) Rotha and Saunders, *ibid.*, **54**, 342 (1932).

(8) The weight of a sample was always the same for any given meal (Table III).

trolled. After the importance of temperature variations was demonstrated, extractions were run at constant temperature.

TABLE II

EFFECT OF TEMPERATURE UPON THE AMOUNT OF NITROGENOUS SUBSTANCE EXTRACTED FROM ORANGE-SEED MEAL BY 4.0 *N* SODIUM CHLORIDE

Temperature, °C.	Total N extracted, %
39.7	48.65
26.0	41.43
−2.5	35.92

The two findings reported above were only incidental to the main problem, namely, to determine how the amount of nitrogen extracted from seed meals would vary with changes in the concentration of the extracting sodium chloride solution which ranged from 0 to saturation. The data (Table III) demonstrate clearly that (1) the most efficient extraction of nitrogenous material occurs when the concentration of the sodium chloride is between 0.25 and 3.0 *N* and (2) even a saturated sodium chloride solution will extract almost as much as a normal solution. Because of this fact, extraction with saturated sodium chloride has been made our standard procedure for the isolation of crystalline globulins, since the extracted material is less likely to be contaminated with gummy substances which interfere with further purification.[9]

TABLE III

EFFECT OF CONCENTRATION UPON THE AMOUNT OF NITROGENOUS SUBSTANCE EXTRACTED FROM VARIOUS SEED MEALS BY SODIUM CHLORIDE

Normality of NaCl soln.	Total N extracted from seed meals, %			
	Flax 3-g. sample	Orange 3-g. sample	Peanut 1.5-g. sample	Rye 5-g. sample
Distilled water	24.27	32.24	52.86	14.81
0.125	41.73	35.59	71.15	20.32
.25	58.63	51.10	91.76	32.45
.375	64.59	58.12	94.85	34.75
.50	64.50	65.54	94.55	34.13
.75	64.48	70.22	93.88	26.69
1.0	64.59	73.34	94.42	25.00
2.0	65.19	72.38	95.37	17.03
3.0	63.75	71.59	94.14	18.57
4.0	61.71	67.62	95.89	14.49
5.0	56.29	67.82	92.26	11.23
6.0	50.12	65.84	87.68	7.65
Saturated	45.53	64.92	81.23	7.65

Discussion

If we make the assumption that most of the nitrogen extracted represents protein, then the data of Table III show that in solutions of sodium chloride greater than 0.5 *N* the concentration of the sodium chloride has little effect upon the solubility of the protein. This assumption is probably justified (except in the case of rye flour) since it can be shown that as much as 90% of the total nitrogen extracted by *N* sodium chloride can be recovered as crystalline globulin (unpublished results) and, as mentioned above, crystalline globulin can be extracted from some seed meals by saturated sodium chloride solutions. The crystalline globulins obtained by extraction with either *N* or saturated sodium chloride solutions have the same crystalline form and give the same analytical figures for total sulfur, total nitrogen and nitrogen distribution.

It has also been shown[7] that *N* solutions of strong bases and weak acids such as sodium benzoate and sodium acetate will extract just as much nitrogen from orange-seed meal as will solutions of salts of strong bases and strong acids.

The data in Table III show that the proteins of rye flour, in which gliadin predominates, show a type of solubility curve entirely different from those of the other three seeds in which globulin predominates. In the case of the rye flour, which contains little or no globulin, the curve rises to a definite peak and then falls off rapidly. In the case of the globulin-containing seeds the curve rises steeply and then remains almost horizontal.

The findings reported above show that the ordinary definitions of globulins are false and misleading, at least by implication. Certainly some globulins are soluble in saturated salt solutions and they are also soluble in solutions of salts of strong bases and weak acids. A satisfactory definition of globulins must take these facts into consideration explicitly.

Several workers have questioned the advisability of basing definitions and classification of proteins on solubility. Staker and Gortner,[10] referring to an earlier paper, state, "Gortner, Hoffman and Sinclair[11] were the first to object to a system of protein classification based upon 'solubility'." These authors[11] also state, "It may be that only 'crystalline' globulins are chemical entities and that the amorphous globulin preparations recorded in the literature are non-homogeneous fractions whose chemical and physical properties depend upon the technic employed in their isolation."

It is interesting to note that McCalla and Rose,[12] working with the gliadin–glutenin system of wheat flour, have also come to the conclusion

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[9] *Cf.* Weyl, *Z. physiol. Chem.*, **1**, 72 (1877); Osborne, *Am. Chem. J.*, **14**, 629 (1892); THIS JOURNAL, **19**, 487 (1897).

[10] Staker and Gortner, *J. Phys. Chem.*, **35**, 1565 (1931).

[11] "Colloid Symposium Monograph," Vol. V, The Chemical Catalog Co., Inc., New York, 1928, p. 179.

[12] McCalla and Rose, *Can. J. Research*, **12**, 346 (1935).

that, "definitions of flour proteins based on solubility in a solution such as 70% alcohol are purely arbitrary." Their work has no bearing on the specific problem of the definition of globulins but is of importance in the general problem of protein classification.

Undoubtedly the solubilities of different proteins are a reflection of the kind and arrangement of their constituent amino acids. Any definition must necessarily be inadequate and empirical until more is known about the composition of proteins.

Conclusions

1. The amount of nitrogenous material extracted from certain seed meals by saturated sodium chloride solutions is almost as large as that extracted by N solutions. In those seed meals where this conclusion is true, the material which is extracted appears to consist almost wholly of a crystalline or hemi-crystalline protein having the characteristics of a globulin.

2. When a solution of given concentration is used for the extraction of nitrogenous material, a marked temperature coefficient is found.

3. The ordinary textbook definitions of globulins do not adequately consider the solubility properties of globulins.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 27, 1936

[A CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Mechanism of Coprecipitation of Anions by Barium Sulfate[1]

BY FRANK SCHNEIDER[2] AND WILLIAM RIEMAN, III

Five theories[3] have been advanced to account for the contamination of precipitates, *viz.*, formation of mixed crystals, occlusion, surface adsorption after the formation of the precipitate, compound formation and postprecipitation. If coprecipitation is defined as the retention of soluble substances by a precipitate, compound formation and postprecipitation cannot be regarded as true coprecipitation. Surface adsorption is important only in the cases of amorphous and flocculent precipitates. Therefore, coprecipitation by barium sulfate is due either to the formation of mixed crystals or to occlusion. By occlusion is meant the adsorption of foreign ions during the growth of the crystals of the precipitate and subsequent entrapping of these foreign ions by the growing crystals.[3]

All conditions of precipitation such as temperature, concentration, time of addition of reagents, time of digestion, etc., being the same, the amount of coprecipitated ion in a precipitate should depend upon some specific property of this ion. As stated by Paneth[4] and Fajans,[5] the occlusion theory maintains that this determining factor is the solubility of the compound formed by the coprecipitated ion and the ion of opposite charge of the precipitate. On the other hand, the mixed-crystal theory of Grimm[6] and coworkers holds that this property is the similarity in crystal structure of the precipitated and coprecipitated substances. Otto Hahn[7] was among the first to recognize that both explanations might be correct. He also stated that mixed crystals may be formed even when Grimm's[8] conditions are not fulfilled. His rules, however, are not very clear and are apparently contradictory in certain respects.

A study of the coprecipitation of various anions by barium sulfate throws considerable light upon this subject. Weiser and Sherrick[9] determined the quantity of coprecipitated anions under identical conditions of precipitation. They did not use the Paneth–Fajans rule to interpret their results and hence were somewhat at a loss to explain them. Sofin[10] repeated their work under more carefully controlled conditions. Using iodide, chloride, bromide, nitrite, nitrate and chlorate, he found that, in accord with the Paneth–Fajans rule, the lower the solubility of the barium

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 92d Meeting of the American Chemical Society, Pittsburgh, September 7–11, 1936.

[2] Abstracted from a thesis by Frank Schneider, presented to the Graduate Faculty of Rutgers University in partial fulfilment of the requirements for the Ph.D. degree.

[3] For a discussion of these theories see Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932).

[4] Paneth, *Physik. Z.*, **15**, 924 (1914).

[5] Fajans and Beer, *Ber.*, **46**, 3486 (1913).

[6] Grimm and Wagner, *Z. physik. Chem.*, **132**, 131 (1928).

[7] O. Hahn, Erzbacher and Feichtinger, *Ber.*, **59**, 2014 (1926).

[8] Grimm, *Z. Elektrochem.*, **30**, 467 (1924).

[9] Weiser and Sherrick, *J. Phys. Chem.*, **23**, 205 (1919).

[10] Sofin, Master's Thesis, Rutgers University, 1934.

salt of the anion, the greater was the amount coprecipitated. The nitrite, however, was an exception. He attempted to show, without success, that the abnormally high amount of coprecipitated nitrite was due to the formation of mixed crystals of sodium nitrite and barium sulfate.

Differences between Occlusion and Mixed-Crystal Formation.—Contamination by occlusion differs from contamination by mixed-crystal formation in the following respects.

(1) As Hahn[7] has pointed out, the extent of occlusion is dependent upon the ion of the precipitate which is present in excess in the solution at the time of precipitation. If barium sulfate is precipitated by adding a sulfate to an excess of barium ion, the growing crystals are charged positively; hence they adsorb and occlude foreign anions to a greater extent than when the precipitate is formed by pouring a barium salt into an excess of sulfate ion. On the other hand, the excess of lattice ion is unimportant in the case of mixed-crystal formation; in this case the contamination is proportional to the concentration of the ion which is coprecipitated.

(2) The adsorptive forces which attract foreign ions to a growing crystal depend primarily on the solubility of the compound which these ions form with the oppositely charged lattice ions. Therefore, contamination by occlusion follows the Paneth–Fajans rule. If the adsorbed ions fit well into the crystal lattice of the precipitate, a larger portion of them is retained by the growing crystals than would otherwise be the case. Therefore, contamination by mixed-crystal formation is greater than the Paneth–Fajans rule indicates. The simple relationship between adsorption and solubility is subject to some exceptions, however. Therefore, deviations from the Paneth–Fajans rule for coprecipitation should not be interpreted as mixed-crystal formation unless the effect of excess lattice ion, the crystal size and the effect of digestion (paragraphs 1, 3 and 4, respectively) also indicate the formation of mixed crystals.

(3) It is well known that the growth of a crystal is retarded by the presence of an adsorbed layer on its surface. If the adsorbed layer can fit into the crystal lattice, however, the retardation is much less than it would be otherwise. Therefore, extensive occlusion causes a fine grained precipitate, whereas contamination by mixed-crystal formation has little effect on crystal size.

(4) Digestion is more effective in removing occluded contamination than in removing mixed-crystal contamination, because the crystals are smaller in the former case, and because their impurities are less uniformly distributed than in the case of mixed crystals.

(5) X-Ray examination may be helpful. It must be emphasized, however, that a small displacement of the lattice dimensions does not indicate that mixed-crystal formation is the sole or even the major cause of the contamination. A given precipitate may be contaminated by both occlusion and mixed-crystal formation.

Application to Coprecipitation of Anions by Barium Sulfate.—As pointed out previously, the amount of nitrite ion coprecipitated by barium sulfate is greater than would be expected from the Paneth–Fajans rule. On the basis of the theory just outlined, it is postulated that (1) iodide, bromide, chloride, chlorate and nitrate ions are coprecipitated by occlusion and (2) that nitrite ion is coprecipitated by the formation of mixed crystals of barium nitrite with barium sulfate. If these postulates are true, it follows that:

(1) The quantity of iodide, bromide, chloride, chlorate and nitrate coprecipitated when the respective barium salt is added to excess sodium sulfate will be much less than when sodium sulfate is added to an excess of the barium salt. In the case of the nitrite, the excess of the precipitating ion will be much less important. The amounts of nitrite coprecipitated will be proportional to the total concentrations of nitrite ion present.

(2) Digestion should be comparatively effective in removing the ions which are occluded but relatively ineffective with the precipitate containing the nitrite.

(3) Extensive coprecipitation of iodide, chloride, bromide, nitrate and chlorate should result in a very fine grained precipitate.

Experimental Work

In order to test this hypothesis, two sets of experiments were carried out. First, barium sulfate was precipitated (a) in the presence of an excess of the barium salt and (b) in the presence of an excess of sodium sulfate. Second, the barium sulfate was precipitated as in the first set of experiments (both a and b) but allowed to digest for a period of twenty-two days before filtering and determining the amount of coprecipitated anion.

Procedure.—Solutions (0.1000 *M*) of barium iodide, bromide, chloride, nitrite, nitrate and chlorate were prepared. A sodium sulfate solution was also made up to

0.1000 *M*. The actual precipitations were carried out as follows: 90 ml. of the barium solution was added to 120 ml. of water; then 40 ml. of the sodium sulfate solution was run in in thirty seconds with vigorous stirring. All solutions were at 30°. Precipitate and solution were allowed to stand for ten minutes after the beginning of precipitation. Separation of solution and precipitate was effected by centrifuging and decanting. The precipitate was washed with 120 ml. of water, and the coprecipitated anion was then determined in the precipitates. The time of centrifuging and washing was carefully controlled to take exactly fifty-five minutes. The experiment was then repeated exactly as before except that 40 ml. of barium salt solution was added to 9 mmol. of sodium sulfate dissolved in 210 ml. of solution.

The precipitates containing iodide, chloride, bromide and chlorate were fused with a carbonate mixture, and the anion was determined in the extract from the melt. The iodide was determined iodometrically, the bromide, chloride and chlorate gravimetrically as the silver salt. The nitrate and nitrite were determined by the method described by Walden and Cohen.[11] In this method the precipitate is digested with a sodium hydroxide–carbonate solution; Devarda's alloy is added; the ammonia is distilled off and countertitrated. In the case of the precipitates formed from barium chloride, the coprecipitated sodium was also determined by the method of Allen and Johnston.[12] The results of this set of experiments are shown in Table I.

TABLE I

Ion	Micromoles of anion per 4 mmol. $BaSO_4$[a] Excess Ba salt	 Excess Na_2SO_4	Ratio	Soly. of barium salt at 30° in moles per 1000 g. water
Iodide	1.3	0.20	6.5	5.64
Bromide	66	14	4.7	3.55
Chloride	107	18	5.9	1.83
Chlorate	390	107	3.6	1.37
Nitrite	408	177	2.3	3.49
Nitrate	783	217	3.6	0.455
Sodium	163	355	1/2.2	

[a] Averages of duplicate determinations. The relative mean deviation was 5% or less except for the iodide, where the relative mean deviation was 20%.

It can be seen that the amount of contaminant increases as the solubility of the barium salt decreases, with the notable exception of the nitrite. The latter is present in an amount far in excess of what would be expected if the solubility of the barium salt were the only determining factor. This indicates that the nitrite is probably coprecipitated by the formation of mixed crystals of barium sulfate and anhydrous barium nitrite and that the other ions are coprecipitated by occlusion. In support of this hypothesis we observed that the precipitate containing 177 micromoles of nitrite ion was much coarser than the precipitates containing 217 micromoles of nitrate ion or 107 micromoles of chlorate ion. Furthermore, the influence of the excess precipitant (barium ion or sulfate ion) was much less in the case of the nitrite ion. Indeed, the observed ratio of 2.3 corresponds surprisingly well to the theoretical value of 9/4 or 2.25 (the ratio of the quantities of nitrite ion used).

Effect of Digestion.—The barium sulfate was precipitated in the same way but was allowed to digest in contact with the mother liquor for a period of twenty-two days at 30° before being centrifuged and analyzed. The results of these experiments compared with the results of the first set are shown in Table II.

TABLE II

Ion		Micromoles of ion per 4 mmol. $BaSO_4$ Before digestion	 After digestion	% Loss
Nitrite				
(A)	Excess of Ba salt	408	160	61
(B)	Excess of Na_2SO_4	177	111	37
Nitrate				
(A)	Excess of Ba salt	783	172	78
(B)	Excess of Na_2SO_4	217	0	100
Chloride				
(A)	Excess of Ba salt	107	42	61
(B)	Excess of Na_2SO_4	18	0	100
Sodium				
(A)	Excess of Na_2SO_4	355	207	42
(B)	Excess of $BaCl_2$	163	110	32

Discussion

The precipitates containing the nitrate and chloride ions lost the impurities more rapidly than the precipitates containing nitrite ion.

Thus it is seen that the nitrite ion behaves differently from the other anions in regard to (1) the Paneth–Fajans rule, (2) the effect of excess lattice ion, (3) the influence on crystal size and (4) the effect of digestion. All these differences support the hypothesis that the nitrite is coprecipitated by mixed-crystal formation, whereas the others are occluded. It is of interest to note that the loss of sodium on digestion indicates that it is held by the barium sulfate in the form of mixed crystals, probably as sodium sulfate.

In connection with the experiments on barium nitrate which showed that the nitrate was present as occluded material, it is of interest to note the recent work of Walden and Cohen.[11] These two authors studied the lattice parameters of precipitates containing coprecipitated nitrate. They have related the lattice parameters to the nitrate content, showing that the parameters increased with increased nitrate content. They concluded, therefore, that the nitrate was present in the form of solid solution or mixed crystals. This conclusion is not supported by our investigation.

Their data unquestionably indicate that mixed crystals were formed to a certain extent, not

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[11] Walden and Cohen, THIS JOURNAL, **57**, 2591 (1935).

[12] Allen and Johnston, *ibid.*, **32**, 588 (1910).

necessarily to a large extent. Walden and Cohen, themselves, realized the possibility that other mechanisms may have played a role in the contamination of their precipitates, for they stated, "That such mechanisms (occlusion or adsorption) may account for a part of the contamination is of course not ruled out by the present investigation, but even this may be questioned because of the remarkably homogeneous and strain-free character of the precipitates." The following considerations indicate that occlusion was probably the major cause of the coprecipitation.

(1) The coprecipitation of 4.53% of nitrate ion increases the volume of the unit cell by only 0.4%. Unless the second component of the mixed crystals (barium nitrate or nitric acid) is unusually similar crystallographically to barium sulfate, a much greater change in the volume of the unit cell is to be expected.

(2) The relationship between the lattice dimensions and the composition differed from linearity more than is to be expected in the case of mixed-crystal formation between salts.

(3) When mixed crystals are in equilibrium with the mother liquor, the partition law is valid.

$$\frac{\text{component A in crystals}}{\text{component B in crystals}} = K\frac{\text{component A in solution}}{\text{component B in solution}}$$

Unless the crystallization is performed extremely slowly, equilibrium may not be established, and the partition law may not be strictly valid. Nevertheless, there is abundant evidence[13] to prove that the mole percentage of the minor constituent in the mixed crystals is dependent primarily on the concentration of this substance in the aqueous solution. On the other hand, Walden and Cohen remark in discussing their results, "A very striking feature of these results, and one hardly to be anticipated, is that the nitrate content of the precipitates is practically independent of the nitrate content of the precipitating solutions. . . . To be noted, however, is the fact that the nitrate content of the precipitates varies with barium ion concentration." These observations are at odds with the hypothesis that mixed-crystal formation is the major cause of the contamination of their precipitates and entirely in harmony with our belief that occlusion was the major phenomenon.

(4) Walden and Cohen remark that extending the range of concentration for further study will have to lead to the use of more dilute solutions since "in the more concentrated range the precipitates settle as muds which are difficult to wash and filter and which give poor X-ray photograms." Since contamination by mixed-crystal formation has only a slight effect on the particle size of the precipitate, the formation of these muds is another indication that the coprecipitation was due chiefly to occlusion.

We conclude, therefore, that occlusion is a more important factor than the formation of mixed crystals in accounting for the contamination of their precipitates.

Summary

(1) Precipitates that are contaminated by occlusion differ from those that are contaminated by mixed-crystal formation in respect to (a) the effect of excess of the lattice ion during precipitation, (b) application of the Paneth–Fajans rule, (c) the size of the crystals and (d) the effect of digestion.

(2) Iodide, bromide, chloride, nitrate and chlorate anions are occluded by barium sulfate, whereas nitrite ion is coprecipitated by mixed-crystal formation. These conclusions are based on the following observations: (a) The excess of lattice ion influences the coprecipitation of nitrite ion much less than it influences the coprecipitation of the other anions. (b) All these anions except the nitrite follow the Paneth–Fajans rule. (c) The size of the crystals of the precipitate is decreased much less by the coprecipitation of nitrite ion than by the coprecipitation of the other anions. (d) The nitrite ion is removed on digestion more slowly than the other anions.

(3) The conclusions of Walden and Cohen are discussed.

NEW BRUNSWICK, N. J. RECEIVED OCTOBER 15, 1936

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[13] Doerner and Hoskins, THIS JOURNAL, **47**, 662 (1925); Henderson and Kracek, *ibid.*, **49**, 738 (1927); Grimm and Wagner, ref. 6; Chlopin, Polessitsky and Tolmatscheff, *Z. physik. Chem.*, **145A**, 57 (1929); Chlopin, Polessitsky, Ratner and Tolmatscheff, *Ber.*, **64**, 2653 (1931); Mumbrauer, *Z. physik. Chem.*, **156A**, 113 (1931); Ratner, Polessitsky and Tolmatscheff, *ibid.*, **A165**, 472 (1933).

[Contribution from the Nutrition Laboratory of the Carnegie Institution of Washington]

The Constancy of the Atmosphere with Respect to Carbon Dioxide and Oxygen Content[1]

By Thorne M. Carpenter

The constancy of the percentages of carbon dioxide and oxygen in uncontaminated atmospheric air was established by Benedict[2] in 1912 by the use of the Sondén[2,3] gas analysis apparatus. As a control upon the correct functioning of the apparatus, analyses of air compressed in a cylinder were made daily along with the analyses of atmospheric air. Only when it was established that the apparatus would give constant results with the compressed air was it found that the composition of the outdoor air was constant. Since that time there has been developed in this Laboratory an apparatus[4] especially for the determination of the changes in the composition of atmospheric air that may be produced by the respiration of animals or of man in a confined space. The apparatus is constructed with a compensating pipet that takes care of the changes in the volume of a gas due to variations in temperature and in atmospheric pressure. The absorption of carbon dioxide is by the use of 10 to 20% potassium hydroxide and the absorption of oxygen takes place by means of potassium pyrogallate solution. The buret is so constructed that readings may be estimated to 0.001% of the volume.

This apparatus has been employed regularly for metabolism experiments which require the use of respiration apparatus and analysis of air samples. Based upon previous work of Benedict,[2] the standardization of the apparatus was made by frequent analysis of atmospheric air. During the course of several investigations, three series have been accumulated in which a control analysis was made on each day that the apparatus was used for experimental purposes.

The first series consists of 75 analyses between August, 1934, and June, 1935, at the Laboratory for Animal Nutrition in the University of New Hampshire. Another series consists of 790 analyses on nearly as many days from January, 1933, to May, 1936, that were made at Baltimore in the Department of Embryology of the Carnegie Institution of Washington, located in the building of the Johns Hopkins Medical School. The third series consists of 291 analyses on the same number of days from June, 1930, to December, 1932, in this Laboratory.

In Table I are given the averages of the analyses in the three series including the standard deviations and ranges for carbon dioxide and oxygen. For carbon dioxide the averages are identical in all three series and the standard deviations have a narrow range of from 0.0015 to 0.0017%. The ranges for the series at Durham and at Boston are practically identical. The range for the carbon dioxide in the series at Baltimore is wide, due to the inclusion of one analysis of 0.060%. Excluding this value, the range for the remaining 789 was 0.028 to 0.033%. The average per cent. of oxygen in the three series is nearly identical with a range of only 0.002% in the three series. The standard deviations for the groups at Durham and at Boston are practically identical. The standard deviation for the group at Baltimore is somewhat larger due to the inclusion of results on twenty-one days that were outside of the range of 20.930 to 20.950%. Of these, 17 were repeated immediately following the aberrant analysis and an average of 20.937% was found with a standard deviation of 0.0027%. The value of 20.926 for the minimum at Durham was exceptional as the range of the other 74 was from 20.933 to 20.948%.

Table I

Averages of Analyses of Atmospheric Air at Durham, N. H., Baltimore, Md., and Boston, Mass.

	No.	Average	S. D.[a]	Range
		Per cent. Carbon Dioxide		
Durham	75	0.031	0.0016	0.027–0.035
Baltimore	790	.031	.0015	.028–0.060
Boston	291	.031	.0017	.026–0.035
		Per cent. Oxygen		
Durham	75	20.939	.0032	20.926–20.948
Baltimore	790	20.938	.0046	20.909–20.957
Boston	291	20.940	.0033	20.931–20.947

[a] S. D. = Standard deviation.

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(1) Presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

(2) F. G. Benedict, "The Composition of the Atmosphere with Special Reference to its Oxygen Content." Pub. No. 166, Carnegie Institution of Washington, 1912.

(3) Sondén, *Z. Instrumentenk.*, **9**, 472 (1889).

(4) Carpenter, *J. Metabolic Research*, **4**, 1 (1923); Carpenter, Fox and Sereque, *J. Biol. Chem.*, **83**, 211 (1929); Carpenter, Lee and Finnerty, *Wiss. Arch. Landw.*, Abt. B., **4**, 1 (1930); Carpenter, Abderhalden's "Handbuch der biolog. Arbeitsmethoden," Abt. IV, T. **13**, 593 (1933).

The division of the series at Baltimore into yearly results is shown in Table II. The averages of the carbon dioxide for the four years are identical and the standard deviations for three years for carbon dioxide are low, whereas the standard deviation for 1936 is somewhat higher due to the inclusion of one aberrant result of 0.060%. The averages for the percentages of oxygen for the four different years have a range of only 0.003%. The standard deviations are under 0.005% for each of the four years.

Table II

Yearly Averages of Analyses of Atmospheric Air at Baltimore

Year	No.	% CO_2	S. D.[a]	% O_2	S.D.[a]
1933	229	0.031	0.0010	20.938	0.0049
1934	230	.031	.0010	20.936	.0044
1935	230	.031	.0012	20.939	.0038
1936	101	.031	.0032	20.938	.0044

[a] S.D. = Standard deviation.

An example of the monthly averages for a single year is given in Table III. The average carbon dioxide ranges from 0.030 to 0.031; thus there was constancy in the percentage of carbon dioxide throughout the year. The monthly standard deviations of carbon dioxide ranged from 0.0010 to 0.0015%. The average of oxygen percentages by months ranged from 20.938 to 20.940%. The range of the standard deviations for the oxygen percentages by months is slightly larger than in the series by years and is due to the occasional finding of an erroneous result which has been included. Thus at Baltimore it was found that the percentages of both carbon dioxide and oxygen were practically constant over a period of nearly four years. A subdivision into months shows that practically the same constancy remains throughout the year.

Table III

Monthly Averages of Analyses of Atmospheric Air at Baltimore, 1935

Month	No.	% CO_2	S. D.[a]	% O_2	S. D.[a]
Jan.	23	0.031	0.0010	20.938	0.0045
Feb.	19	.031	.0011	20.939	.0041
Mar.	23	.030	.0010	20.940	.0038
April	22	.030	.0015	20.939	.0046
May	22	.031	.0011	20.939	.0034
June	21	.031	.0011	20.939	.0043
July	22	.031	.0014	20.940	.0041
Aug.	3	.031	...	20.940	...
Sept.	18	.031	.0015	20.938	.0033
Oct.	21	.031	.0011	20.939	.0033
Nov.	18	.031	.0012	20.939	.0032
Dec.	18	.031	.0012	20.939	.0070

[a] S. D. = Standard deviation.

The yearly averages of the analyses at Boston are shown in Table IV. The carbon dioxide percentages are identical for the three years with a value of 0.031%. Similarly the oxygen percentages are practically constant and the standard deviations by years for the oxygen percentages in the series in Boston are under 0.004% for each year. An example of the monthly averages is given in Table V for the year 1931 at Boston.

Table IV

Yearly Averages of Analyses of Atmospheric Air at Boston

Year	No.	% CO_2	S. D.[a]	% O_2	S. D.[a]
1930	79	0.031	0.0016	20.940	0.0032
1931	135	.031	.0017	20.939	.0032
1932	77	.031	.0017	20.940	.0034

[a] S. D. = Standard deviation.

Table V

Monthly Averages of Analyses of Atmospheric Air at Boston for Year 1931

Month	No.	% CO_2	S. D.[a]	% O_2	S. D.[a]
Jan.	5	0.031	0.0011	20.941	0.0022
Feb.	17	.031	.0011	20.939	.0023
Mar.	8	.032	.0014	20.939	.0024
April	12	.032	.0017	20.940	.0033
May	7	.031	.0016	20.938	.0033
June	16	.030	.0017	20.940	.0037
July	14	.031	.0016	20.940	.0025
Sept.	5	.032	.0013	20.939	.0012
Oct.	14	.031	.0015	20.939	.0026
Nov.	18	.032	.0021	20.940	.0037
Dec.	19	.031	.0020	20.938	.0038

[a] S. D. = Standard deviation.

No analyses were made in August. The carbon dioxide percentages average from 0.030 to 0.032%, the standard deviation ranging from 0.0011 to 0.0021%. The averages of the oxygen percentages range from 20.938 to 20.941%, the standard deviation ranging from 0.0012 to 0.0038%. Thus the composition of the atmospheric air at Boston with respect to its carbon dioxide and oxygen content was practically constant for the period of time covering nearly three years and a subdivision into monthly groups does not increase the range of the averages.

The laboratory in New Hampshire is located on the college campus and is not far from a heavily wooded section. The laboratory at Boston is situated about 200 feet (61 meters) from a heat, light and power plant. There are two stacks of 180 feet (55 meters) and 190 feet (58 meters) each and the total fuel consumption varies from 35 to 95 tons of coal per day. In spite of the widely different local conditions of the three laboratories there is no evidence that variations in season or proximity of large consumers of fuel cause any measurable differences in carbon dioxide and oxygen content of the atmospheric air. As pointed out by Benedict,[2] many of the atomic weights are not known beyond the fourth significant figure, but here is a physical mixture of gases, with the percentage content of one of its constituents, namely oxygen, having a constancy beyond the accuracy of many atomic weight determinations.

The analyses were made at Durham by Mrs. H. H. Latimer and Mr. N. F. Colovos, at Baltimore by Mr. K. Koudelka, and at Boston by Mr. E. L. Fox.[5]

[5] Died Dec. 19, 1934.

Summary

Three series of samples of outdoor air consisting of 75 at Durham, New Hampshire, 790 at Baltimore and 291 at Boston were analyzed for carbon dioxide and oxygen content by means of an apparatus on which readings are estimated to 0.001%. Each series was scattered over nearly the same number of days as there were analyses. The grand average of all three series gave 0.031% for carbon dioxide and 20.939% for oxygen. In spite of widely different local conditions of the three laboratories there was no evidence that variations in season or proximity of large consumers of fuel caused any measurable differences in carbon dioxide and oxygen content of atmospheric air.

BOSTON, MASS. RECEIVED NOVEMBER 23, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Note on the Relative Partial Molal Heat Content of Zinc Sulfate in Aqueous Solution

BY HERBERT S. HARNED

Cowperthwaite and La Mer[1] have measured the electromotive forces of the cells

Zn(2-phase amalgam) | $ZnSO_4(m)$ | $PbSO_4$-Pb(2-phase amalgam)

at concentrations from 0.0005 to 0.01 *M*, and from 0 to 50° at 12.5° intervals. They showed that these results were in conformity with the Gronwall, La Mer and Sandved[2] extension of the Debye and Hückel theory, provided that 3.64 Å. was used for the mean distance of approach of the ions, *a*. With this equation, they obtained the standard potentials of the cell at the temperatures at which they were measured.

From these data, La Mer and Cowperthwaite[3] have computed the relative partial molal heat content, $\overline{L}_2$. This quantity has also been obtained from calorimetric data by Lange, Monheim, and Robinson,[4] who derived values which differed considerably from those computed from the electromotive forces. Such a discrepancy detracts from the value of Cowperthwaite and La Mer's proof of the validity of the extended theory unless it can be shown that this disagreement disappears upon further consideration of the results.

Following Cowperthwaite and La Mer, we shall employ the quantity E_0', defined by the equation of the cell by

$$E_0' = E + \frac{\gamma RT}{NF} \ln m = E_0 - \frac{\gamma RT}{NF} \ln \gamma \quad (1)$$

where E is the measured electromotive force corrected for lead sulfate solubility, E_0 the standard potential of the cell, and the other symbols have their usual connotation. The calculation of $\overline{L}_2$ by La Mer and Cowperthwaite is open to two criticisms. In the first place, they employed a five constant power series equation ending in a term containing T^4 to express five results. If one or more of the results are in error, this procedure will not yield an accurate temperature coefficient at a given temperature. Secondly, their results at 50° were obtained with difficulty and in fact seem to be inconsistent with the results at the lower temperatures. Electromotive force measurements as a function of temperature usually may be expressed with high accuracy by a quadratic equation. To test this in the present instance, the first order differences of Cowperthwaite and La Mer's results[1] were plotted against T. These plots are straight lines with the exception of the one which involves the 50° reading, a fact which indicates that a quadratic equation may

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[1] Cowperthwaite and La Mer, THIS JOURNAL, **53**, 4333 (1931).

[2] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[3] La Mer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933).

[4] Lange, Monheim and Robinson, *ibid.*, **55**, 4733 (1933).

be used to compute E'_0 from 0 to 37.5°. In Table I are given the constants of the equations

$$E' = E'_{25} + a'(t - 25) + b'(t - 25)^2 \qquad (2)$$

and

$$E_0 = E_{0(25)} + a'(t - 25) + b'(t - 25)^2 \qquad (3)$$

where E_0 is the standard potential. These equations will express the results with an average deviation of 0.07 mv. in regions of concentration from 0.001 to 0.01 M, inclusive. The 0.0005 M result is not so good, but the values of E_0 from the extrapolation of Cowperthwaite and La Mer agree with those computed by equation (3) to within 0.05 mv. On the absolute temperature scale these equations become

$$E'_0 = a + bT + cT^2 \qquad (4)$$

$$E_0 = a_0 + b_0T + c_0T^2 \qquad (5)$$

from which $\overline{L}_2$ in calories may be computed as shown by Harned and Thomas[5] by

$$\overline{L}_2 = -46{,}118\ [(a - a_0) - (c - c_0)T^2] \qquad (6)$$

The values of a were smoothed by plotting against m. In Table I, values of $(a - a_0)$, $(c - c_0)$ and $\overline{L}_2$ computed by this method are collected. In the eighth column are given the values of this quantity calculated by Lange, Monheim and Robinson from their heat of dilution data. The agreement between the values derived from these two types of measurement is good, particularly since an error of 0.001 mv. per degree in the temperature coefficient of electromotive force causes an error of 14 cal. in $\overline{L}_2$. Further, since an error of 0.1 in the estimation of $(c - c_0) \times 10^7$ produces an error of 41 cal., the discrepancy at 0.0005 M is not serious. Indeed, it is hardly likely under the most favorable circumstances that $\overline{L}_2$ can be estimated from these results with an accuracy greater than 30 cal. In the last column of the table the results of La Mer and Cowperthwaite's calculation are given. As the concentration increases, there is an increasing deviation between their results and those derived from heat of dilution data which amounts to 200 cal. at 0.01 M. At 0.0005 M, La Mer and Cowperthwaite's value checks the calorimetric, but as previously mentioned this may not be significant since the whole computation is so sensitive and since the electromotive force data are less consistent at this concentration.

TABLE I

$\overline{L}_2$ OF ZINC SULFATE. CONSTANTS OF EQUATIONS (2), (3) AND (6)

m	$E_{0(25)}$	$(-a'_0 \times 10^3)$	$(-b'_0 \times 10^6)$					
0.0	0.41087	1.106	4.00	....		...	...	...
	E'_{25}	$(-a' \times 10^3)$	$(-b' \times 10^6)$	$(a - a_0)$	$(c - c_0) \times 10^7$	$\overline{L}_2$, e. m. f.	$\overline{L}_2$, cal.	$\overline{L}_2$ La M.
0.0005	0.41725	1.085	3.93	0.0019	0.7	(198)	255	266
.001	.42002	1.052	3.87	.0032	1.3	385	355	395
.002	.42365	1.025	3.82	.0055	1.8	480	492	563
.005	.42989	1.005	3.76	.01024	2.4	674	676	812
.01	.43524	0.980	3.68	.01525	3.2	772	790	978

Summary

By employing a quadratic equation to express the electromotive force data of the cell[1] Zn (2-phase amalgam) | $ZnSO_4(m)$ | $PbSO_4$-Pb (2-phase amalgam) from 0 to 37.5° with the omission of an uncertain result at 50°, values of the relative partial molal heat content of zinc sulfate were computed. These values are in agreement with those obtained by measurements of heats of dilution,[4] a fact which seems to justify our method of procedure. We may conclude that from 0 to 37.5° the electromotive force data possess a high accuracy which we judge to be of the order of ±0.05 mv. If the method here employed is correct, the previous discrepancy between the values of $\overline{L}_2$ obtained from heat data[4] and electromotive force measurements[3] disappears. This agreement is excellent evidence for Cowperthwaite and La Mer's extrapolation of the electromotive forces, and lends confirmation to their proof of the effect of the extended terms of the Debye and Hückel theory.

NEW HAVEN, CONN. RECEIVED DECEMBER 12, 1936

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(5) Harned and Thomas, THIS JOURNAL, **58**, 761 (1936).

[CONTRIBUTION FROM THE UNIVERSITY OF BRITISH COLUMBIA]

Systems of Sulfur Dioxide and the Isomeric Xylenes

BY W. F. SEYER, K. MARTIN AND L. HODNETT

A number of systems of sulfur dioxide and aromatic compounds have been studied. Thus Znozzetti and De Carli measured the freezing points of sulfur dioxide and benzene solutions and claimed to have obtained evidence showing the existence of three compounds.[1] In later publications F. De Carli states he had obtained compounds of sulfur dioxide with toluene, ethylbenzene and certain other derivatives of benzene. He made no mention of having investigated the three xylenes and, as it was of interest to know whether the three xylenes behaved in a similar manner with the solvent sulfur dioxide, a series of freezing point measurements were made on the three systems.

Materials.—The organic compounds used were obtained from Kahlbaum. As the ortho, meta and para xylenes were the purest available, no further purification beyond distilling over sodium was attempted. The sulfur dioxide was the usual C. P. variety supplied by Baker and Co. in little iron tanks. Before condensation, the gas was bubbled through dilute sulfuric acid to remove any sulfur trioxide, then through several wash bottles of concentrated acid and over phosphorus pentoxide to remove any traces of water.

Procedure.—The bulb method was used throughout as it was the most convenient and was considered to be sufficiently accurate for the results desired. Various amounts of the hydrocarbons were introduced into a series of bulbs by means of a thin-stemmed thistle tube. The bulbs, whose volumes averaged about 2.5 cc. and whose stems were about 20 cm. in length, were then capped and weighed to obtain the amount of xylene. Definite quantities of sulfur dioxide were next condensed in these tubes which were then sealed and weighed. The amounts of xylene and sulfur dioxide could thus be obtained directly, and as a check, the sulfur dioxide content was always determined after the freezing point had been found, by titration with sodium hydroxide.

Sulfur dioxide was introduced into the bulbs in two ways. In the case of *p*-xylene, the apparatus described in Vol. 23, p. 327, of the *J. Ind. Eng. Chem.* was used. Bulbs, containing weighed amounts of *p*-xylene, were cooled until the contents froze and they were then sealed onto the filling line. The air was removed by a mercury vapor pump (the xylene being kept frozen in the meantime) after which the desired amounts of sulfur dioxide were condensed in each bulb. It was found that if the air were not sufficiently removed, the contents of the bulbs became red and finally dark in color when allowed to attain room temperature. In the absence of air, however, solutions of any one of the xylenes and sulfur dioxide remained clear and colorless even after standing for some months at room temperatures.

In the case of ortho and meta xylene, whose freezing points are much lower than that of the para compound, a simpler method of filling the bulbs was found to be equally successful. All that was required was to cool the bulb containing the xylene, first sweep out the air with sulfur dioxide and then by further cooling cause the gas to condense. It was found that the amount of xylene vapor lost during the removal of the air was negligible.

The next step was to determine the freezing point of the solution in each bulb. A bath, containing 95% alcohol and a little ether, was set up in a Dewar tube and connected to a container from which liquid air was blown to cool the bath. A pentane thermometer, a platinum resistance thermometer, standardized by the Bureau of Standards, and one of the bulbs were placed in the bath. The temperature was slowly lowered by the liquid air until crystals appeared in the solution in the bulb. The temperatures on the thermometers were noted and the bath was allowed to warm slowly until only one or two crystals remained. The temperature was kept at this level for several minutes, or as long as there was no apparent increase or decrease in the size or number of crystals. The bath was then allowed to warm slightly and the point at which the crystals disappeared was taken as the freezing point. Because of the viscosity of the solutions it was difficult to stir the contents of the bulbs thoroughly; this of course affected the freezing point of the solution, hence reported freezing points would vary as much as one degree. The results recorded in Table I are the averages of three determinations. The freezing point of sulfur dioxide was taken as 75.43°.

TABLE I

p-XYLENE AND SULFUR DIOXIDE

p-Xylene, g.	Sulfur dioxide, g.	Sulfur dioxide, mol %	F. p., °C.
0.3998	0.0326	11.86	+ 8.9
.9009	.0872	13.81	+ 6.9
2.4287	.2435	14.20	+ 4.8
2.3583	.2767	16.27	+ 4.3
1.1742	.2325	24.67	+ 0.8
0.6574	.1447	26.71	− 1.1
.7376	.2294	33.99	− 6.1
.7152	.3503	44.75	−12.9
.4734	.2858	49.99	−17.6
.7422	.6067	57.52	−26.3
.5409	.6001	61.36	−29.3
.8552	.9192	63.93	−34.1
.7631	1.1330	71.07	−41.4
.3963	1.0023	80.70	−51.2
.2668	0.8867	84.70	−57.6
.1087	.5693	89.90	−64.2
.1596	8.0000	98.90	−76.8
.0412	10.9005	99.77	−75.9

Freezing point of *p*-xylene +13.2°.

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[1] C. Znozzetti and F. De Carli, *Gazz. chim. ital.*, **56**, I, 34–36 (1926).

TABLE II

o-XYLENE AND SULFUR DIOXIDE

o-Xylene, g.	Sulfur dioxide, g.	Sulfur dioxide, mol %	F. p., °C.
2.6440	0.1362	7.88	−31.0
0.9209	.0466	7.73	−31.2
1.7261	.2005	16.13	−34.4
0.7073	.1086	20.27	−36.5
.7585	.1298	22.08	−36.8
.9992	.3604	37.39	−41.2
.8724	.3921	42.67	−44.3
.3944	.2238	48.44	−47.5
.8109	.6969	58.69	−51.4
.6172	.5927	61.33	−53.0
.3099	.4853	72.11	−60.0
.0894	.2537	82.58	−66.1
.2714	1.4259	89.87	−72.0
.4684	3.0402	91.50	−72.7
.0398	0.6235	97.00	−77.0
.0524	1.2478	97.70	−78.1
.0685	2.5360	98.39	−78.3
.0318	1.5661	98.82	−78.7
.0223	2.4350	99.45	−76.4

Freezing point of *o*-xylene −27.1°.

TABLE III

m-XYLENE AND SULFUR DIOXIDE

m-Xylene, g.	Sulfur dioxide, g.	Sulfur dioxide, mol %	F. p., °C.
1.1390	0.0804	10.30	−54.9
1.8307	.3257	22.52	−57.4
1.2469	.3937	34.26	−59.8
1.0973	.8057	54.82	−64.0
1.1060	.9064	57.55	−64.7
0.8079	1.2128	71.32	−68.1
.4032	0.8916	78.62	−70.7
.4172	1.9854	88.89	−73.5
.2213	1.7839	93.07	−75.5
.1949	1.9730	94.78	−76.4
.3205	4.2585	95.65	−76.6
.1032	6.1136	98.99	−76.9
.1356	9.8676	99.18	−76.2
.1063	11.9383	99.46	−75.7

Freezing point of *m*-xylene −53.6°.

The data when plotted as curves in Fig. 1 show each system to have only one entectic. Thus there is no indication of compound formation. To further test this point crystals of the hydrocarbons which formed from solutions containing varying amounts of sulfur dioxide were analyzed but with unsatisfactory results.

By utilizing the well-known equation

$$\ln N = \frac{-L}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

the values of the latent heat of fusion were calculated. These are given in Table IV and compared with those measured directly.

TABLE IV

LATENT HEAT OF FUSION OF THE XYLENES

	Calculated	Temperature range, °C.	Found
p-Xylene	3560 cal.	13.2– 0.8	4168[a] cal.
o-Xylene	3550	−27.1−−42	3333[b]
m-Xylene	6317	−53.6−−57.4	2760[b]

[a] "International Critical Tables." [b] Rossini, *Bur. Standards J. Research,* **11**, 553–559 (1933).

It thus appears that the *o*-xylene and sulfur dioxide behave very nearly as ideal solutions but this is not so in the case of the two others, the *p*-xylene deviating positively and the *m*-xylene negatively from the ideal solution.

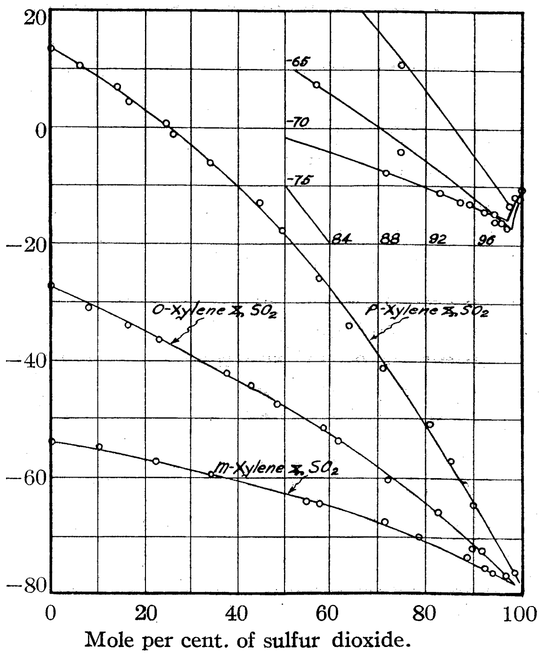

Fig. 1.

Summary

1. The freezing point curves of para, ortho and meta xylenes with sulfur dioxide have been constructed from freezing point data. There appears to be no compound formation, as there is only one eutectic in each case.

2. The calculated latent heats of fusion when compared with the experimental values show the para and meta solutions to deviate considerably from the ideal.

VANCOUVER, B. C.

RECEIVED NOVEMBER 23, 1936

[Contribution from the Chemical Laboratory of The Ohio State University]

The Beta to Alpha Conversion of Fully Acetylated Sugars by Alkali

By M. L. Wolfrom and Donald R. Husted

In some work carried out in this Laboratory on a reaction involving *β-d*-glucose pentaacetate, it was found that this *β*-form had been isomerized unexpectedly to *α-d*-glucose pentaacetate. This change was obtained under conditions entirely different from those recorded in the literature for effecting the conversion of a fully acetylated *β*-form of a sugar to the corresponding *α*-isomer. Such a conversion had been produced previously by treating the *β*-pentaacetate in acetic anhydride solution with either zinc chloride[1] or sulfuric acid;[2] or by treatment with stannic chloride in chloroform.[3] The experimental conditions which we found effective for producing this conversion were studied in considerable detail in order to determine the agent producing the change. We believe that the effective agent was a very mild alkalinity. This is in contrast to the acidic conditions previously used to cause the shift. This result can be harmonized with modern theories of sugar mutarotation, since both acidic and basic catalysts are effective in the transformation of a non-substituted reducing sugar into its *alpha* and *beta* forms.[4]

The procedure used by us was to shake a solution or suspension of the completely acetylated *β*-form of the sugar in a suitable non-aqueous solvent with solid sodium hydroxide and a suitable drying agent. Anhydrous and alcohol-free ether as well as dioxane were found to be suitable solvents but were most effective when used in an equal mixture. No difference was found in the action of commercial or highly purified dioxane. Either sodium or anhydrous calcium sulfate (Drierite) was suitable as drying agent, such an agent apparently being required to protect the reaction mixture from becoming too alkaline. The sodium hydroxide was essential. These conditions are those of incipient alkaline deacetylation and some deacetylation always occurred. Consequently, this reaction is not the equal of the previously established methods for preparative purposes, but we believe that it is of theoretical interest, particularly in its relation to the study of the interconversion of isomeric sugar structures.

The reaction was extended successfully to *β-d*-mannose pentaacetate, *β-d*-galactose pentaacetate and *β*-lactose octaacetate.

Experimental

***α-d*-Glucose Pentaacetate.**—An amount of 25 cc. of dry dioxane (a high grade commercial product dried with sodium or anhydrous calcium sulfate (Drierite)) and 25 cc. of diethyl ether (anhydrous and alcohol-free) were placed in a citrate pressure bottle and approximately 3 g. of sodium and 3 g. of crushed, solid sodium hydroxide were added. This mixture was shaken mechanically for approximately fifteen minutes and then 3 g. of pure *β-d*-glucose pentaacetate was added quickly and the mixture shaken for a period of four to six hours. Some dark brown sludge formed and the solution was colored brown. After a little experience the completeness of the reaction could be judged by this color. At the end of the shaking, some Carboraffin was added and the mixture rapidly filtered with suction into a flask containing a few cc. of acetic acid. The acidified filtrate was light yellow in color and showed a specific rotation varying from +70 to +90°. The residue obtained after solvent removal under reduced pressure was crystallized from 95% ethanol (Carboraffin), the first crop of crystals being *α-d*-glucose pentaacetate of good purity; m. p. 110–111° (unchanged on admixture with known material of the same purity); $[\alpha]$ +96°[5] ($CHCl_3$); average yield approximately 1.2 g., maximum 1.5 g.; acetyl, 13.0 cc. 0.1 *N* NaOH per 100 mg. (calcd., 12.8 cc.). After several recrystallizations the following constants were obtained: m. p. 112–113°; $[\alpha]^{22}$ +98.5° (*c*, 3; $CHCl_3$). Hudson and Dale[6] record for *α-d*-glucose pentaacetate the constants: m. p. 113°; $[\alpha]^{20}$ +101.5° ($CHCl_3$).

When the conditions described above were adhered to rigidly, no *β*-form was isolated from the reaction. If the reaction was stopped short of completion, some *β*-form could be isolated. After a little experience, the results described above could be obtained in about 90% of the trials, the limitations being that if the reaction was stopped short of the optimum point some *β*-form was obtained, while if the reaction was allowed to proceed too far or if too much moisture was accidentally introduced, deacetylation resulted.

It was thought at first that the rearrangement might have been effected by impurities contained in the dioxane but no difference was noted when dioxane was used that had been purified by the method of Kraus and Vingee.[7]

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[1] (a) E. Erwig and W. Koenigs, *Ber.*, **22**, 1464 (1889); (b) C. S. Hudson and J. M. Johnson, This Journal, **37**, 1270 (1915).

[2] L. Maquenne and W. Goodwin, *Bull. soc. chim.*, [3] **31**, 854 (1904); Edna Montgomery and C. S. Hudson, This Journal, **56**, 2463 (1934).

[3] E. Pacsu, *Ber.*, **61B**, 137 (1928).

[4] T. M. Lowry and G. F. Smith, "Rapports sur les Hydrates de Carbone," Dixième Conférence de l'Union Internationale de Chimie, Liége, 1930, pp. 79–121.

[5] All of the recorded rotations were measured to the D-line of sodium.

[6] C. S. Hudson and J. K. Dale, This Journal, **37**, 1264 (1915).

[7] C. A. Kraus and R. A. Vingee, *ibid.*, **56**, 511 (1934).

This point was settled satisfactorily when it was found that ether alone could be used as a solvent if the time of shaking was prolonged to from eighteen to twenty-four hours. Purified dioxane could also be used alone but then the reaction likewise proceeded at a very slow rate. The sodium used in the procedure served merely as a drying agent, since anhydrous calcium sulfate (Drierite) could be substituted for it without affecting the yield. When sodium was used and the solid sodium hydroxide omitted, a very low yield of α-glucose pentaacetate was obtained. This small amount of conversion was undoubtedly due to the slight quantity of sodium hydroxide produced by unavoidable contamination with moisture. All of these experiments pointed to the conclusion that the active interconverting agent was the sodium hydroxide. When α-*d*-glucose pentaacetate was used initially, it was recovered unchanged in approximately 50% yield but no β-form was isolated. This would indicate either that the equilibrium was displaced to favor the α-form or that the β-isomer was more readily deacetylated.

α-*d*-Galactose Pentaacetate.—Pure β-*d*-galactose pentaacetate (3.0 g.) was treated exactly as described for β-*d*-glucose pentaacetate except that the time of shaking was from five to seven hours. The acidified filtrate showed a specific rotation of from +60 to +80°. The sirup obtained after solvent removal under reduced pressure was dissolved in ethanol, treated with Carboraffin, filtered and the ethanol removed under reduced pressure. The residual sirup was dissolved in chloroform and the solution washed successively with 5% hydrochloric acid, 5% aqueous sodium bicarbonate and then with water, dried, the solvent removed under reduced pressure and the residual sirup crystallized from a small amount of hot ethanol; yield 0.8 to 1.0 g.; m. p. 94–95° (mixed m. p. unchanged); $[\alpha]^{27}$ +104° (*c*, 3.7; $CHCl_3$). Hudson and Parker[8] record for α-*d*-galactose pentaacetate the constants: m. p. 96°; $[\alpha]^{20}$ +107° ($CHCl_3$).

α-*d*-Mannose Pentaacetate.—Pure β-*d*-mannose pentaacetate (3.0 g.) was treated exactly as described for β-*d*-glucose pentaacetate except that the time of shaking was from four to four and one-half hours. The acidified filtrate showed a specific rotation of approximately +45°. The sirup obtained after solvent removal was crystallized from hot water; yield 1.2 g.; m. p. 73–74°; $[\alpha]^{33}$ +59° (*c*, 2.6; $CHCl_3$; 2-dm. semimicro tube). After one further recrystallization the substance showed the constants: m. p. 74–75° (mixed m. p. unchanged); $[\alpha]^{28}$ +60° (*c*, 3.3; $CHCl_3$; 2-dm. semimicro tube). Levene and Bencowitz[9] record for α-*d*-mannose pentaacetate the constants: m. p. 75°; $[\alpha]^{22}$ +55° ($CHCl_3$).

α-Lactose Octaacetate.—Pure β-lactose octaacetate (3.0 g.; m. p. 90°; $[\alpha]$ −4.2°, $CHCl_3$) was treated exactly as described for β-*d*-glucose pentaacetate and the sirup obtained after solvent removal was dissolved in ethanol (Carboraffin) and the ethanol removed under reduced pressure. The residual sirup was triturated with several portions of cold water and obtained crystalline from either ethanol or ether by slow evaporation of the solvent. α-Lactose octaacetate is difficult to crystallize and the yield was very low; m. p. 149–150°; $[\alpha]^{21}$ +51° (*c*, 2.9; $CHCl_3$; 2-dm. semimicro tube). On one further recrystallization the melting point was 152° (mixed m. p. unchanged). Hudson and Johnson[1b] record for α-lactose octaacetate the constants: m. p. 152°; $[\alpha]^{20}$ +54° ($CHCl_3$).

Summary

1. A method was found for converting β-*d*-glucose pentaacetate to the α-form, using sodium hydroxide as the reagent.

2. The method was extended to the corresponding fully acetylated derivatives of *d*-galactose, *d*-mannose and lactose. It is probably of general application.

COLUMBUS, OHIO RECEIVED NOVEMBER 19, 1936

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[8] C. S. Hudson and H. O. Parker, THIS JOURNAL, **37**, 1589 (1915).

[9] P. A. Levene and I. Bencowitz, *J. Biol. Chem.*, **72**, 627 (1927)

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

The Configurations of α- and β-*p*-Bromobenzophenone Oximes

BY RAYMOND WRIGHT JOHNSON AND JOE GOLENTERNEK

An earlier contribution by Johnson and Stieglitz[1] from this Laboratory reported the details of an empirical method for the determination of the velocity of hydrolysis of oximes. Data were reported which showed that the individual members of the pair of stereoisomeric oximes of *p*-methylbenzophenone hydrolyzed at considerably different rates.

The purpose of this study was, first, to test the generality of this difference in rates by the investigation of another pair of stereoisomeric oximes and, second, to extend the study to include a comparison of the rates of hydrolysis of the stereoisomeric forms with those of the corresponding symmetrical oximes. It was hoped that this might throw some light on the configurations of the stereoisomeric compounds. The compounds selected were the α and β forms of *p*-bromobenzophenone oxime and the related oximes of benzophenone and *p,p'*-dibromobenzophenone.

Preparation of Materials

Benzophenone Oxime.—This compound was prepared by the method of Fischer.[2]

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[1] Johnson and Stieglitz, THIS JOURNAL, **56**, 1904 (1934).

[2] Fischer, "Anleitung zur Darstellung organ. Prepärate," Braunschweig, 1908, p. 68.

***p,p′*-Dibromobenzophenone Oxime.**—A mixture of the ketone (10 g.) and hydroxylamine hydrochloride (6.5 g.) dissolved in ethyl alcohol (700 cc. of 95%) to which a solution of sodium carbonate (10 g. in 30 cc. of water) had been added was refluxed on a steam-bath for ten hours and then allowed to cool. The unreacted ketone (about 25% of the original amount) and sodium carbonate was removed by filtration. The filtrate was diluted with water (2500 cc.) and chilled. Crystals of the crude oxime (7.5 g., m. p. 140–145°) were obtained. Two recrystallizations from ligroin (b. p. 90–100°) produced the pure oxime (m. p. 150–152°).

Anal. (Micro) Calcd. for $C_{13}H_9ONBr_2$: N, 3.94. Found: N, 3.94, 4.02.

α- and β-*p*-Bromobenzophenone Oximes.—Anhydrous sodium acetate (100 g.) was added to a solution of the ketone (50 g.) and hydroxylamine hydrochloride (60 g.) in ethyl alcohol (400 cc. of 95%). The mixture was refluxed for six hours on a steam-bath. The alcohol was removed by distillation and the residue was washed several times with warm water. The crude mixture of the two oximes (51 g.) when dry had a melting point of 102–160°. The method used for the separation of the two forms was based on the difference in their solubility in solutions of sodium hydroxide. The crude mixture of oximes was extracted with successive portions (700, 150, 85 and 50 cc.) of a hot (90°) solution of sodium hydroxide (2 *N*). The undissolved oxime (m. p. 160–165°) on recrystallization from ethyl alcohol produced the pure α-oxime. The melting point of this pure α-form (m. p. 168–170°) was higher than that reported (165–166°) previously by Schäfer.[3] The combined alkaline extract was saturated with carbon dioxide gas to precipitate the oxime in solution. This material was washed with water until free from alkali. The dried material was dissolved in hot ethyl alcohol (absolute). Fractional crystallization was obtained by means of the addition of small quantities of water from time to time. Relatively small amounts of the pure β-form (m. p. 109–111°) were obtained.

Anal. (Micro) Calcd. for $C_{13}H_{10}ONBr$: N, 5.07. Found: (α-form), N, 5.01, 4.93; (β-form), 5.03, 4.88.

Method

The method used for the determination of the velocity of hydrolysis of the oximes was essentially that of Johnson and Stieglitz.[1] The limited solubility of these bromo compounds in an acetic–hydrochloric acid mixture such as was used by them required the use of a mixture richer in acetic acid. This necessitated a slight change in the extraction procedure. The procedure followed in each of the determinations listed below was identical. A weighed quantity of the oxime was dissolved in glacial acetic acid (140 cc. of reagent quality) at 25° in a 200-cc. graduated flask. At a definite noted time exactly 50 cc. of hydrochloric acid (1.899 *N*) at 25° was run in. The volume of the solution was quickly made up to 200 cc. by the addition of glacial acetic acid. After it was thoroughly mixed, the solution was placed in a thermostat at 25 ± 0.02°. From time to time a sample (25 cc.) of the solution was pipetted into a Squibb separatory funnel. At a definite noted time 35 cc. of water was added and the procedure from that point on was the same as that described by Johnson and Stieglitz.[1] The concentration of the oxime in the various determinations ranged from 0.03 to 0.045 *N*.

Tests with known solutions showed that this procedure yields quantitative results with acetic–hydrochloric acid solutions of hydroxylamine such as were obtained in this investigation.

The fact that the reactions in each case were normal and yielded only the respective ketone and hydroxylamine was proved when examinations of the content of completely hydrolyzed solutions yielded only these two substances.

Results

The average of at least two determinations of the velocity of hydrolysis of each of the oximes studied is given in Table I.

TABLE I

VELOCITY OF HYDROLYSIS OF OXIMES (25°)

Compound, oxime	Concn. of HCl in hydrolyzing solution, *N*	$K \times 10^5$
Benzophenone	0.4747	60.21
α-*p*-Bromobenzophenone	.4747	67.49
β-*p*-Bromobenzophenone	.4747	55.85
p,p′-Dibromobenzophenone	.4747	46.83

Discussion

In the article by Johnson and Stieglitz[1] the hydrolysis of oximes tentatively was assumed to consist of at least two consecutive reactions, the first reaction consisting of the addition of a molecule of water to the double bond between carbon and nitrogen in the oxime or its salt, followed by the decomposition of this intermediate hydrated form to produce the normal end products. Furthermore, it was pointed out that, if such is the true mechanism for the reaction, the experimentally determined rate of hydrolysis of the stereoisomeric oximes must be that of the addition of water to form the intermediate hydrated compound. The data reported in this paper are most logically explained by this theory. The fact that the rate of hydrolysis of chloral oxime[4] is very much less than the rate of hydrolysis of the hydrate of chloral oxime supports this general theory.

If this simple mechanism is valid, and, if *cis* addition of the molecule of water takes place, one might expect that that one of the two stereoisomeric oximes investigated which has the *syn*-phenyl configuration would hydrolyze at a rate more nearly approximating the rate of hydrolysis of benzophenone oxime than the rate for *p,p′*-dibromobenzophenone oxime. Similarly of the two the rate of hydrolysis of the form with the *syn-p*-bromophenyl configuration might be ex-

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[3] Schäfer, *Ann.*, **264**, 152 (1891).

[4] Unpublished data.

pected to approximate more nearly the rate of hydrolysis of *p,p'*-dibromobenzophenone oxime. An examination of the data in Table I shows that the rate of hydrolysis of α-*p*-bromobenzophenone oxime more nearly approximates the rate for benzophenone oxime than it does that for *p,p'*-dibromobenzophenone oxime. Thus this criterion of configuration would assign the *syn*-phenyl configuration to the α-*p*-bromobenzophenone oxime. Similarly, the closer relationship between the rates of hydrolysis of the β-*p*-bromobenzophenone oxime and *p,p'*-dibromobenzophenone oxime would assign the *syn-p*-bromophenyl configuration to the β-*p*-bromobenzophenone oxime. These configurations agree with those assigned to the α- and β-forms of this oxime by the method of Hantzsch, based on the products of the Beckmann rearrangement of the individual oximes. However, if *trans* addition of water occurs, the interpretation of the above data would reverse the assigned configurations. Thus no claim can be made for the validity of this method until further investigations have been made on other pairs of oximes. In particular data on the rates of hydrolysis of oximes whose configurations have been determined by other means are needed. This work will be done in this Laboratory.

Summary

1. The velocities of hydrolysis of benzophenone oxime, *p,p'*-dibromobenzophenone oxime and the stereoisomeric α- and β-*p*-bromobenzophenone oximes were determined under identical conditions.

2. A possible tentative method for the assignment of configurations to stereoisomeric oximes, based on a comparison of velocity of hydrolysis constants, is discussed.

CHICAGO, ILL. RECEIVED SEPTEMBER 28, 1936

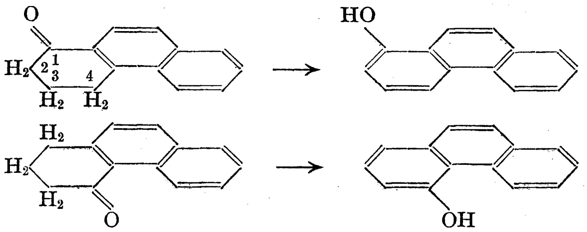
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XIV. The Preparation of 1- and 4-Phenanthrol

BY ERICH MOSETTIG AND HARRY M. DUVALL[1]

As starting material for the synthesis of new compounds which might possess oestrogenic activity, we were in need of several of the phenanthrols. While all five of the possible monohydroxyphenanthrenes are known, heretofore there has been no satisfactory method of preparing the 1- and 4-isomers. The total synthesis of 1- and 4-methoxyphenanthrene by Pschorr's method[2] can hardly be considered for large scale preparation. The synthesis of the 1-hydroxy- and in particular of the 4-hydroxyphenanthrene by the pyrolysis of α- and β-naphthylparaconic acid,[3] respectively, appears quite impracticable. The more recent preparations of 1-phenanthrol by potassium hydroxide fusion of the rare 1-sulfonic acid[4] and by diazotization of 1-aminophenanthrene[5] do not appear feasible.

In a previous communication of this series[6] we stated that 1-phenanthrol can be obtained from 1-keto-2-bromo-1,2,3,4-tetrahydrophenanthrene in a yield of about 50% by elimination of hydrogen bromide, while 4-phenanthrol is obtained only in small amounts by an analogous reaction. A more direct way, however, appeared to be dehydrogenation of the 1- and 4-ketotetrahydrophenanthrenes themselves, according to the scheme



The principle of this method is not new and has been applied successfully by Darzens and Levy[6,7] in the preparation of phenols from the corresponding hydroaromatic ketones, using sulfur and selenium as dehydrogenating agents. Since we found the application of these agents to the ketotetrahydrophenanthrenes not very successful,

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(1) E. R. Squibb and Sons Research Fellow.

(2) (a) Pschorr, Wolfes and Buckow, *Ber.*, **33**, 162 (1900); (b) Pschorr and Jäckel, *ibid.*, **33**, 1826 (1900).

(3) (a) Shoesmith and Guthrie, *J. Chem. Soc.*, 2332 (1928); (b) Behrend and Ludewig, *Ann.*, **379**, 351 (1911).

(4) Fieser, THIS JOURNAL, **51**, 2460 (1929).

(5) Bachmann and Boatner, *ibid.*, **58**, 2194 (1936).

(6) Mosettig and Burger, *ibid.*, **57**, 2189 (1935).

(7) Darzens and Levy, *Compt. rend.*, **194**, 181 (1932); Levy, *ibid.*, **194**, 1749, 1952 (1932). See also Ruzicka, *Helv. Chim. Acta*, **19**, 419 (1936); Fieser, Hershberg and Newman, THIS JOURNAL, **57**, 1509 (1935).

a systematic investigation on catalytic dehydrogenation was carried out with respect to solvent, time of reaction, catalyst and amount of catalyst, which finally enabled us to prepare 1- and 4-phenanthrol in yields of 68–86% and 56–63%, respectively. As the ketotetrahydrophenanthrenes are relatively accessible,[8] this method appears to be a convenient approach to the hitherto rare 1- and 4-phenanthrol. Furthermore, we found that, with the exception of the few cases noted in Table I, the ketotetrahydrophenanthrene which was not converted to phenanthrol can be recovered nearly quantitatively.

TABLE I

DEHYDROGENATION OF 1-KETO-1,2,3,4,-TETRAHYDROPHENANTHRENE[a]

Dehydrogenating agent	Solvent[i]	Time of refluxing, hrs.	Yield of Phenanthrol,[o] %
0.10 g. Pd[b]	Tetralin[j]	24	38
0.10 g. Pd	Xylene	3	10
0.10 g. Pd	Xylene	24	38
0.10 g. Pd	Xylene	48	53
0.10 g. Pd	Xylene	96	70
0.20 g. Pd	Xylene	24	63
0.10 g. Pd	Naphthalene	24	86[p]
0.10 g. Pd	Naphthalene[k]	48	68
ca. 2 g. Ni[c]	Xylene	8	8
ca. 4 g. Ni	Xylene	24	38
ca. 6 g. Ni	Naphthalene	24	27
0.20 g. PtO_2[d]	Tetralin[j]	24	41
0.20 g. PtO_2	Xylene	24	40
0.12 g. PtO_2	Naphthalene	24	73
0.10 g. PdO[e]	Xylene	24	0
1.00 g. Pd charcoal[f]	Xylene	24	0
0.10 g. Pd + 5.0 g. safrole[g]	Xylene	24	0
0.54 g. S	Naphthalene[l]	3	35
1.34 g. Se[h]	Naphthalene[l]	3	0

DEHYDROGENATION OF 4-KETO-1,2,3,4,-TETRAHYDROPHENANTHRENE

Dehydrogenating agent	Solvent	Time of refluxing, hrs.	Yield of Phenanthrol, %
0.10 g. Pd	Tetralin[j]	0.5	Negligible
0.10 g. Pd	Xylene	3	5
0.30 g. Pd	Xylene	24	57[p]
0.20 g. Pd	Xylene	120	47
0.10 g. Pd	Naphthalene[m]	24	18
0.10 g. Pd	Phenanthrene[m,n]	24	0
0.10 g. Pd	Benzene	72	Negligible
ca. 6 g. Ni	Xylene	24	2
0.10 g. PdO	Xylene	24	0
0.20 g. PtO_2	Xylene	24	0
0.54 g. S	Naphthalene[l]	3	17

[a] All runs listed in the table were made on 3.00-g. batches of ketotetrahydrophenanthrene. [b] Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 123 (1921). [c] Raney catalyst, Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932). [d] Adams, Vorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 452. [e] Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924). [f] In the proportion 0.14 g. palladium on 0.86 g. charcoal. Ott and Schröter, *Ber.*, **60**, 633 (1927). [g] Compare Akabori and Suzuki, and Akabori and Saito, *Proc. Imp. Acad.* (Japan), **5**, 255 (1929); **6**, 236 (1930); *C. A.*, **23**, 4671 (1929); **24**, 5037 (1930). [h] See experiment without solvent, Mosettig and Burger, ref. 6. [i] All solvents were dried and purified by refluxing and distilling over sodium. [j] This solvent was chosen in view of the dehydrogenation experiments of Kindler and Peschke, *Arch. Pharm.*, **272**, 236 (1934). It is noteworthy that when platinum oxide catalyst was used, all of the ketotetrahydrophenanthrene which had not been dehydrogenated to phenanthrol could be recovered, but when palladium black catalyst was used, only about half of the expected ketotetrahydrophenanthrene could be recovered, indicating that with the latter catalyst side reactions had taken place (possibly hydrogenation by means of the fixed hydrogen of the tetralin). [k] An unidentified by-product (0.4 g.), insoluble in ether and in alkali, and sparingly soluble in benzene, melting with decomposition at about 340°, was obtained. [l] No attempt was made to work up the non-phenolic part of the reaction products. [m] No ketotetrahydrophenanthrene could be recovered. The formation of water was observed in both cases. It is very likely that phenanthrene was formed; see Cook and Hewett, *J. Chem. Soc.*, 403 (1933), who obtained phenanthrene on selenium dehydrogenation of 4-ketotetrahydrophenanthrene. [n] A by-product (1.5 g.) insoluble in ether and in alkali, but moderately soluble in benzene, melting without decomposition at 306–309°, was obtained. It is probably identical with the compound, m. p. 312°, which Cook and Hewett[m] obtained as a by-product from the selenium dehydrogenation of 4-ketotetrahydrophenanthrene. [o] The figures in this column represent the yield of about 90–95% pure phenanthrol. [p] These conditions were adopted as most satisfactory for the preparation of the phenanthrols in larger quantities. Thus, in two runs on 10.0-g. batches of 1-ketotetrahydrophenanthrene, using 0.33 g. of palladium black catalyst, we obtained yields of 82 and 84%. These yields were obtained using portions of the same catalyst. With another catalyst, prepared from the same stock of palladium chloride, the yield dropped to 68%, apparently because of uncontrollable factors in the preparation of the catalyst. 4-ketotetrahydrophenanthrene was dehydrogenated in two 25.0-g. batches, using 3.30 g. of palladium black catalyst, whereby yields of 56 and 63% were obtained.

We plan to subject the phenanthrols, in part continuing previous work,[9] to the Friedel and Crafts reaction, using various acid chlorides and anhydrides, which should give us a variety of hydroxy carbonyl compounds, including those containing a fourth ring.

Experimental Part

Dehydrogenation Experiments.—The ketotetrahydrophenanthrene was refluxed with the catalyst in ten parts

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(8) Haworth, *J. Chem. Soc.*, 1125 (1932); Fieser and Peters, THIS JOURNAL, **54**, 4354 (1932); Martin, *ibid.*, **58**, 1438 (1936).

(9) Mosettig and Burger, THIS JOURNAL, **55**, 2981 (1933); Burger and Mosettig, *ibid.*, **56**, 1745 (1934).

by weight of solvent. The catalyst was recovered from the reaction mixture, either by filtration of the latter, if liquid at room temperature, or by filtration of an ethereal solution of the reaction mixture. The reaction solvent was removed either by distillation under reduced pressure or by steam distillation, after removal of the ether. The residue from these distillations was then warmed for about fifteen minutes with an excess of 5% potassium hydroxide solution, and the undissolved material taken up in ether. Four or five extractions of the ethereal solution with alkali removed practically all of the phenanthrol. The alkaline extracts were combined with the first alkaline solution and acidified with concentrated hydrochloric acid, whereupon the phenanthrol separated in a crystalline state. From the residue of the ethereal solution the unreacted ketotetrahydrophenanthrene may be recovered as its semicarbazone. The results of some of the experiments are summarized in Table I.

1-Phenanthrol.—Pure 1-phenanthrol was obtained from the dehydrogenation product by one distillation at 1 mm., followed by sublimation; m. p. 153–154°.

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.56; H, 5.19. Found: C, 86.21; H, 5.16.

The acetate and the methyl ether melted at 134–135° and 103–104°, respectively. The melting points agree with the corresponding values given in the literature.[2a,3a,4,6]

4-Phenanthrol.—4-Phenanthrol was purified in the same manner as the 1-isomer, and melted at 113–115°, in agreement with the value given by Mosettig and Burger.[6]

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.56; H, 5.19. Found: C, 86.44; H, 5.55.

The acetate and methyl ether melted at 58–59.5° and 67–68°, respectively, in agreement with the values given in the literature.[2b,3b]

Summary

1- and 4-phenanthrol have been prepared in yields of 68–86% and 56–63%, respectively, by the catalytic dehydrogenation of 1- and 4-keto-1,2,3,4-tetrahydrophenanthrene.

UNIVERSITY, VIRGINIA RECEIVED JANUARY 2, 1937

[CONTRIBUTION NO. 48 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Chemical Constitution of a Bituminous Coal as Revealed by its Hydrogenation Products

BY BURNARD S. BIGGS[1] AND J. F. WEILER

In earlier contributions from this Laboratory[2] it was shown that both the extract and the residue from the extraction of a Pittsburgh seam coal with benzene at 260°, yielded, upon high pressure hydrogenation at 350° with a copper–calcium chromite catalyst, 80% of their carbon as petroleum ether soluble oils essentially hydrocarbon in nature. Boiling points, refractive indices and hydrogen–carbon ratios indicated that these hydrocarbons were partially hydrogenated polycyclic aromatic compounds. Because of (1) the nature of the catalyst employed, which is particularly effective in breaking cyclic and linear ether oxygen linkages, (2) the moderate temperatures used, which preclude appreciable degradation of hydrocarbon structures and (3) the large fraction of the carbon of the original coal converted, it appears that these oils properly may be regarded as fundamental units of the coal in the sense that the coal structure may be considered as built of such units combined through peripheral functional groups.

In this paper are presented the results so far obtained in the characterization of these oils. The oils recovered from the preliminary hydrogenation with copper–calcium chromite were completely saturated by hydrogenation over Raney nickel catalyst, then fractionally distilled and the fractions characterized through their boiling points, refractive indices, molecular weights and hydrogen–carbon ratios.

Experimental.—Both the residue and the extract from the extraction of Edenborn[3] coal with benzene at 260° were hydrogenated over Adkins catalyst by the stepwise procedure described by Biggs[2b] in which hydrogenation, followed by removal of petroleum ether soluble oils, was repeated until there was practically complete conversion to oils. From 200 g. of residue there was obtained in seven steps 24.5, 21.7, 18.6, 20.4, 26.5, 12.6 and 9.2 g., or a total of 133.5 g. of petroleum ether soluble oils containing 79.7% of the carbon of the starting materials. From 100 g. of extract there was obtained in five steps 21.5, 26.7, 19.5, 12.8 and 4.7 g., or a total of 85.2 g. of petroleum ether soluble oils representing 87% of the carbon of the original extract. The accumulated products in each case were then dissolved in benzene and subjected to a final hydrogenation over Adkins catalyst at 280° for twenty-four hours. After removal of benzene the product was dissolved in cyclohexane and subjected to hydrogenation over 10% of Raney nickel catalyst at 220° and 1800 pounds (120 atm.) initial hydrogen pressure until the absorption of hydrogen had ceased. This necessitated cooling the bomb

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[1] Now located at Summit, N. J., Bell Telephone Laboratories.

[2] Biggs, THIS JOURNAL, (a) 58, 484 (1936); (b) 58, 1020 (1936).

[3] U. S. Bureau of Mines Tech. Paper No. 525 (1932).

TABLE I

COMPARISON OF THE PROPERTIES OF SOME KNOWN HYDROAROMATIC COMPOUNDS WITH VARIOUS FRACTIONS OF THE HYDROGENATION PRODUCTS OF THE RESIDUE (R) AND EXTRACT (E) FROM THE BENZENE PRESSURE EXTRACTION OF A BITUMINOUS COAL

No.[a]	Grams	Mol %	Wt. %	Initial atm. b. p., °C.	n^{25}_D	Mol. weights[b]		Empirical formulas			H/C
						Catechol	Diphenyl	C	H	OH	
R_1	3.0	6.9	2.2	190	1.467	122	128	8.7	15.6	0.34	1.83
R_2	5.4	11.1	4.0	205	1.482	146	144	10.0	17.1	.33	1.74
R_3	2.5	4.2	1.9	230	1.494	175	177	12.5	20.6	.32	1.67
R_4	5.5	8.2	4.1	262	1.509	195	198	14.1	22.5	.29	1.61
R_5	2.5	3.4	1.9	315	1.524	198	218	15.6	23.8	.26	1.54
R_6	15.9	18.6	11.8	320	1.540	244	252	18.2	27.2	.30	1.51
R_7	17.9	15.6	13.3	395	1.563	330	338	24.6	33.2	.42	1.37
R_8	16.4	10.8	12.1	450	1.593	405	448	33	44	.42	1.35
R_9	51.6	21.2	38.2	...	...	520	720	53	64	.75	1.21
Loss	14.3		10.6								
E_1	10.8	26.7	13.0	220	1.498	165	170	12	19.3	.34	1.63
E_2	7.7	14.5	9.2	315	1.533	218	224	16	24.0	.30	1.52
E_3	16.5	23.6	19.6	385	1.567	275	295	21.5	29.7	.36	1.39
E_4	3.0	3.5	3.6	440	1.594	377	357	26.4	35.9	.29	1.34
E_5	10.3	10.2	12.2	460	1.613	384	427	31.4	38.1	.38	1.23
E_6	35.7	21.5	42.5	...	...	...	...	..	..	...	..
Deca(per)hydronaphthalene				185	1.468	138		10	18	...	1.80
Tetradeca(per)hydrophenanthrene				(250)[c]	1.499	192		14	24	...	1.71
Dodecahydrophenanthrene				268	1.508	190		14	22	...	1.57
Octadeca(per)hydrochrysene				360	1.521	246		18	30	...	1.68
Hexadecahydrochrysene				(380)	1.541	244		18	28	...	1.55
Octadeca(per)hydrotriphylene				...	1.518(n^{25}_{α})	246		18	30	...	1.68
Hypothetical compound with 7 rings				400	...	320		24	34	...	1.41

[a] Nos. R_1–R_5 are from the refractionation of a fraction taken off at atmospheric pressure. No. R_9 is the residue remaining in the still. No. E_6, non-distillable in the conventional apparatus, was further distilled in a molecular still, but with partial decomposition so that analytical data for this fraction are not available. [b] Reproducible to 1 part in 10. [c] Atmospheric boiling points given in brackets are estimated from values given for lower pressures.

after five hours in order to replenish the hydrogen. The total time at 220° was approximately ten hours. The oils from both the extract and the residue absorbed from 2–3 g. of hydrogen per 100 g. of oil. That hydrogen absorption had not ceased due to poisoning of the catalyst was established by the activity of the catalyst in a subsequent hydrogenation of benzene at 180°. The resulting products were freed of cyclohexane on a water-bath and then fractionally distilled at 1 mm. pressure up to a temperature of 350°.

Microanalyses for carbon and hydrogen were made on all fractions; molecular weights were determined cryoscopically in both catechol and diphenyl according to the method of Smith and Howard,[4] and the initial atmospheric boiling points and refractive indices were noted. The presence of some oxygen in the lower boiling fractions led to the estimation of hydroxyl contents by acetylation with acetic anhydride in pyridine solution.[5]

Results and Conclusions

The properties of the various fractions of the oils obtained by hydrogenation of residue and extract are given in Table I. For the purpose of comparison the properties of some known hydroaromatic compounds are given at the bottom of the table. That these fractions represent a true range of building units and not various degrees of polymerization or association of some unit or units is indicated by the close agreement of the values for the molecular weights determined in catechol and in diphenyl. In the undistilled fraction, R_9, there was some divergence which would indicate that this fraction had not been depolymerized completely. However, a further hydrogenation of this fraction at 280° for forty-eight hours produced only traces of material distilling below 400°.

An interesting point is the hydroxyl content of these supposedly hydrocarbon substances. Hydroxyl oxygen accounts for from 70–90% of the "oxygen by difference." The constant molar hydroxyl content for the various fractions from both the residue and extract suggests that oxygen-containing groups have entered into the coalification process in some systematic manner. Although the replacement of hydrogen by hydroxyl in a hydrocarbon raises the refractive index

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[4] Smith and Howard, THIS JOURNAL, **57**, 512 (1935).

[5] Freed and Wynne, *Ind. Eng. Chem., Anal. Ed.*, **8**, 278 (1936).

slightly, the hydroxyl content of this material is sufficiently small to permit the drawing of valid conclusions concerning the nature of the hydrocarbons present from a comparison with known hydrocarbons.

If properties of known hydroaromatic compounds are compared with those of the various fractions, we find that of the residue fractions, R_1 and R_2, limpid water white liquids, correspond rather closely to decalin; R_3 and R_4, light yellow slightly viscous liquids, correspond to dodeca- and tetradecahydrophenanthrene; and R_5 and R_6, golden yellow very viscous liquids of marked tackiness, correspond to hexadeca- and octadecahydrochrysene. The inclusion of dodecahydrophenanthrene and hexadecahydrochrysene, compounds lacking two hydrogen atoms of complete saturation, in the list of completely saturated compounds for comparative purposes is justified because of the great difficulty of introducing these last two hydrogen atoms. Due to lack of data on known compounds of more than four condensed rings, we can only surmise from the regular increase in boiling points and refractive indices and from molecular weight and composition that fractions R_7, R_8 and R_9 were composed of larger members of the type assigned to the lower fractions. Thus, in molecular weight and hydrogen–carbon ratio fraction R_7 and a hypothetical seven-ring compound were nearly identical.

The fractionation of the product from the extract was not so close as that of the product from the residue and consequently we find fraction E_1, a yellow oily liquid, corresponds roughly to a mixture of decalin and the hydrophenanthrenes; fraction E_2, a yellow very viscous tacky oil, corresponds to the hydrochrysenes; and fraction E_3, a yellow resinous substance, corresponds to a hypothetical seven-ring compound.

Despite evident overlapping, it is concluded that the respective fractions are composed chiefly of the polycyclic hydrocarbons, and their isomers and homologs, to which they are found to correspond in the above comparison. Although chiefly hydrocarbon in nature, each fraction has a hydroxyl content equivalent on the average to one hydroxyl group per three hydrocarbon molecules. That coals of lower rank contain fundamental structural elements of a cyclic nature has been indicated by the fact that low temperature (290–400°) serial hydrogenation of a brown coal in presence of MoS_3 was found[6] to yield benzine and kerosene fractions consisting predominantly of aromatic and naphthenic hydrocarbons.

An approximate distribution of the various sized building units in the residue and in the extract is summarized in Table II. Although there is present in both materials upward of 50% by weight of building units of molecular weight of approximately 700, the calculated average molecular weight in both cases is about 300. This compares with the results of Smith and Howard,[4] who found molecular weights ranging from 200–300 for humic acids prepared by the oxidation of Edenborn coal.

TABLE II

APPROXIMATE DISTRIBUTION OF BUILDING UNITS IN THE EXTRACT AND RESIDUE ACCORDING TO THE NUMBER OF CONDENSED RINGS PRESENT IN THE UNITS

No. of rings	Residue		Extract	
	Mol. %	Wt.[a] %	Mol. %	Wt. %
2	18	7	27	13
3	12	7		
4	22	15	15	9
5–7	16	15	27	23
?>7	32	56	32	55

[a] Corrected for loss.

The agreement found for the distribution of units in residue and extract is further evidence in support of the viewpoint that the benzene insoluble and soluble parts of this coal differ more in the size of the polymeric aggregate than in essential chemical structure.[2b]

While in this study the general constitution and distribution of the building units in this coal have been shown, further evidence as to the exact nature of these substances is extremely desirable. The catalytic dehydrogenation of these hydroaromatic oils to the corresponding aromatic compounds to permit isolation and identification through addition compounds such as picrates is being studied in this Laboratory.

Summary

By catalytic hydrogenation, first over Adkins catalyst at 350°, and then over Raney nickel catalyst at 220°, approximately 80% of the carbon of the extract and of the residue from the benzene extraction of a Pittsburgh seam coal at 260° has been converted to hydroaromatic oils which may be regarded as the hydrocarbon skeletons of the building units in the respective materials.

Fractionation of these oils followed by charac-

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[6] Djakova and Lozovoi, *Compt. rend. Acad. Sci., U. R. S. S.*, **2**, 254 (1935).

terization of the fractions through their molecular weights, boiling points, refractive indices and hydrogen–carbon ratios has given an approximate distribution of the various sized units in the extract and in the residue.

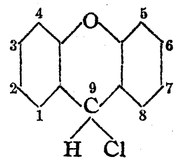
Pittsburgh, Penna. Received December 18, 1936

[Contribution from the Chemistry Laboratory of the University of Michigan]

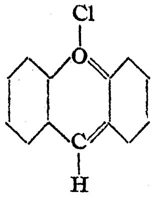
The Reaction between Triarylmethyl Halides and Phenylmagnesium Bromide. III. 9-Phenylxanthyl Chloride[1]

By C. S. Schoepfle and J. H. Truesdail

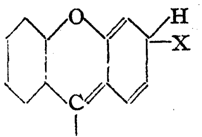
In 1901, Werner[2] found that xanthenol gave a colored solution with hydrochloric acid and concluded that a colored xanthyl chloride was formed. Since the benzenoid structure (I) would not account for the color of this salt, he accepted the oxonium structure (II) which had been assigned to such compounds the year before by Hewitt.[3] Bünzly and Decker[4] later prepared phenylxanthenol which likewise formed colored salts with mineral acids to which they assigned oxonium structures. Neither Werner nor Bünzly and Decker obtained the pure chlorides but they were able to isolate colored addition products with metallic salts such as ferric chloride and mercuric chloride. Xanthyl chloride and phenylxanthyl chloride were first prepared in pure form by Gomberg and Cone[5] and found to be colorless. With dry hydrochloric acid gas, however, phenylxanthyl chloride gave a red addition product containing one molecule of hydrogen chloride. The color observed by Werner and by Bünzly and Decker when xanthenols were treated with hydrochloric acid was, therefore, not due to the chlorides but to the chloride–hydrochlorides which were formed.



I

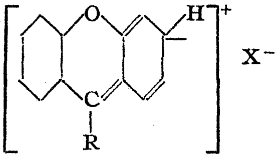


II



III

or



IV

X = $Cl \cdot HCl$, $Cl \cdot FeCl_3$, etc.

Gomberg and Cone assigned a quinonoid structure (III) to the colored addition products of xanthyl chlorides because of the close agreement in the properties of these compounds with the corresponding addition products of the triarylmethyl halides. One of the many arguments cited in favor of the quinonoid structure of the latter compounds was the fact that a bromine atom in the para position in bromotriphenylmethyl chloride is labile and is readily replaced when shaken with silver chloride in a sulfur dioxide solution,[6] while a bromine atom in the ortho or meta position is not replaced under any conditions. The same situation was found to exist with the xanthyl halides.[5] If the bromine atom in bromophenylxanthyl halides was in the 3-position, it was readily replaced by chlorine either by shaking with silver chloride in a benzene solution containing a small amount of hydrogen chloride, or merely by treating with excess of dry hydrochloric acid gas at room temperature. However, the bromine atom could not be replaced if it was in the phenyl group which is not a part of the xanthene ring, which showed that the phenyl group does not become quinonoid.

Further evidence that triarylmethyl halides can exist in two modifications was obtained from the reaction of triphenylchloromethane with phenylmagnesium bromide,[7] where the chloride reacts partly in the benzenoid form to give tetraphenylmethane (usually 5–8% yield), and partly in the quinonoid form to give biphenyldiphenylmethane (50–80% yield).[8] In the present paper it is shown that 9-phenylxanthyl chloride likewise reacts in two forms with phenylmagnesium bromide.

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(1) From the Ph.D. dissertation of J. H. Truesdail.

(2) Werner, *Ber.*, **34**, 3300 (1901).

(3) Hewitt, *Z. physik. Chem.*, **34**, 1 (1901); *Ber.*, **34**, 3819 (1901).

(4) Bünzly and Decker, *ibid.*, **37**, 2931 (1904).

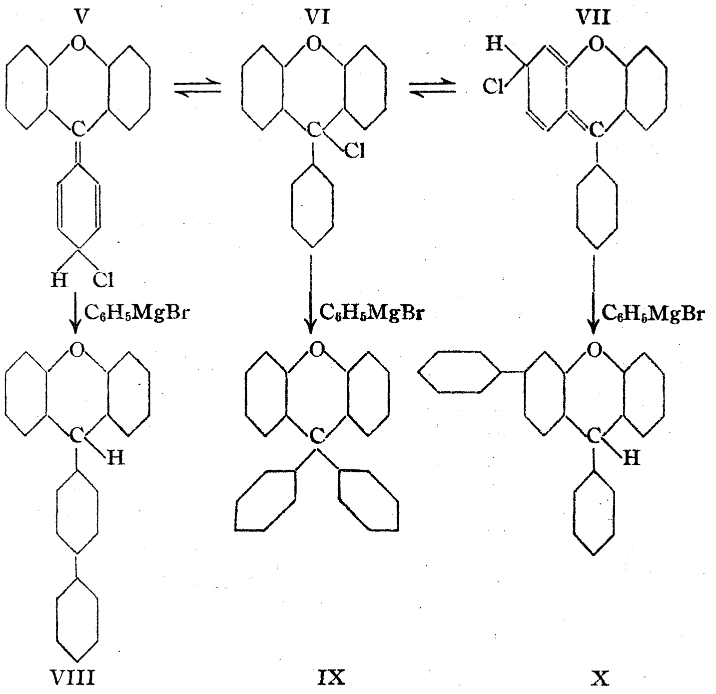
(5) Gomberg and Cone, *Ann.*, **370**, 142 (1909); *ibid.*, **376**, 183 (1909).

(6) Gomberg, *Ber.*, **40**, 1861 (1907).

(7) Gilman and Jones, This Journal, **51**, 2840 (1929).

(8) Schoepfle and Trepp, (a) *ibid.*, **54**, 4059 (1932); (b) *ibid.*, **58**, 791 (1936).

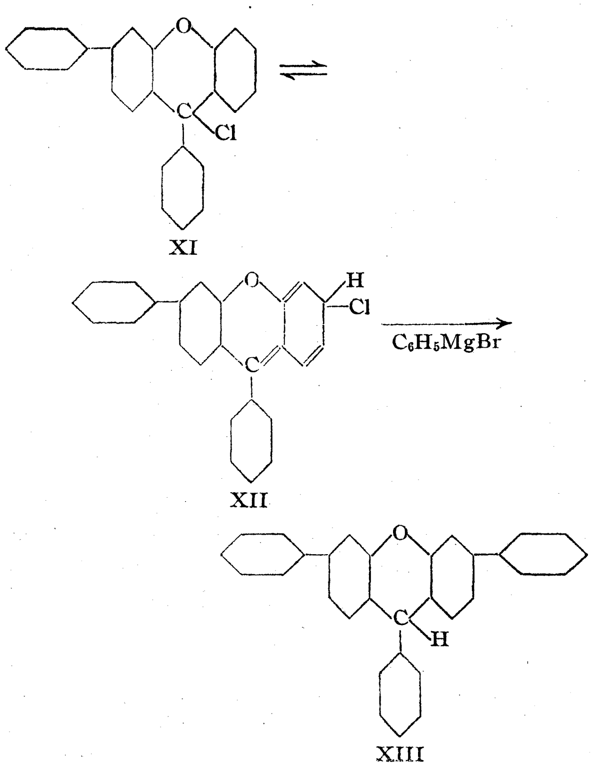
Theoretically, it is possible for 9-phenylxanthyl chloride to exist in a benzenoid modification (VI), and in two quinonoid modifications, one in which the 9-phenyl group assumes a quinonoid structure (V), and the other in which part of the xanthene ring assumes a quinonoid structure (VII). If the benzenoid form (VI) reacts with phenylmagnesium bromide, 9,9-diphenylxanthene (IX) will be obtained. However, if the quinonoid form (V) reacts, the replacement of the chlorine atom by the phenyl group gives an intermediate unstable molecule which will rearrange to 9-biphenylxanthene (VIII). Finally, if the quinonoid form (VII) reacts, then the intermediate compound obtained will rearrange to give 3,9-diphenylxanthene (X).



Only two of these three compounds were actually isolated from the reaction between 9-phenylxanthyl chloride and phenylmagnesium bromide, namely, 9,9-diphenylxanthene (IX) in traces, and 3,9-diphenylxanthene (X) in 34–51% yield. In addition, however, there were obtained 3,6,9-triphenylxanthene (XIII) in 3–14% yield and 9-phenylxanthene in 13–21% yield. (The variations in yields are due no doubt to experimental difficulty in isolating the crystalline compounds rather than to variations inherent in the reaction itself.)

3,6,9-Triphenylxanthene and 9-phenylxanthene evidently are secondary rather than primary products of the reaction. Corresponding compounds were obtained in small amounts in the reaction of triphenylchloromethane and phenylmagnesium bromide, and their formation was explained by assuming an intermolecular oxidation–reduction reaction between unreacted triphenylchloromethane and the primary reaction product, biphenyldiphenylmethane.[8b] In the present case, a similar explanation is offered. During the course of the reaction, a part of the 3,9-diphenylxanthene at the moment of formation (or the intermediate compound from which the xanthene is obtained) reacts with unchanged 9-phenylxanthyl chloride to give 9-phenylxanthene and 3,9-diphenylxanthyl chloride (XI). The latter compound will now react further with phenylmagnesium bromide and, by analogy with 9-phenylxanthyl chloride, it should react mainly in the quinonoid form (XII) to give 3,6,9-triphenylxanthene (XIII).

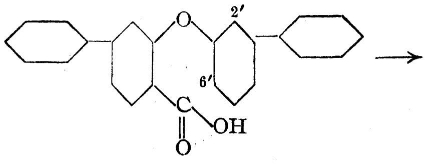
It has been found that in the reaction of triphenylchloromethane with phenylmagnesium bromide,[8b] the magnesium bromide present in solution favors the formation of the



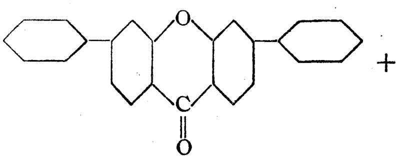
quinonoid modification. This effect is shown clearly by the fact that a much higher yield of tetraphenylmethane may be obtained if triphenylchloromethane is allowed to react with diphenylmagnesium[9] in place of phenylmagnesium bromide. Magnesium bromide should induce an even higher concentration of the quinonoid modification of 9-phenylxanthyl chloride than of triphenylchloromethane, since the former becomes quinonoid more readily than the latter. However, because only a small amount of 9,9-diphenylxanthene and a large amount of 3,9-diphenylxanthene are obtained in the reaction of phenylmagnesium bromide with 9-phenylxanthyl chloride, it must not be inferred that the chloride exists principally in the quinonoid form. Instead, the probable explanation is that the rate of reaction of the benzenoid form of 9-phenylxanthyl chloride with phenylmagnesium bromide is exceedingly slow in comparison to the rate of reaction of the quinonoid form. At present, the relative rates of reaction cannot be determined because of the disturbing effect of the magnesium bromide on the equilibrium between the two forms. It is of interest to note that no 9-biphenylxanthene was isolated in the reaction, indicating that the phenyl group does not become quinonoid, which is in agreement with the results of Gomberg and Cone who found that halogens in the phenyl group were not labile.

In order to identify the products of the reaction between 9-phenylxanthyl chloride and phenylmagnesium bromide, it became necessary to synthesize 3,9-diphenylxanthene and 3,6,9-triphenylxanthene. Acetyl-4-aminobiphenyl was chlorinated in acetic acid solution and the product hydrolyzed to give 3-chloro-4-aminobiphenyl.[10] The position of the chlorine atom in this compound was established definitely by a synthesis in which diazotized 3-chloro-4-nitroaniline was coupled with benzene to give 3-chloro-4-nitrobiphenyl which was reduced to 3-chloro-4-aminobiphenyl. The products from the two procedures were identical. The Sandmeyer reaction was used to prepare 3-chloro-4-cyanobiphenyl from 3-chloro-4-aminobiphenyl and the cyanide hydrolyzed to 2-chloro-4-phenylbenzoic acid. The remaining steps in the synthesis of 3,9-diphenylxanthene were the preparation of 2-phenoxy-4-phenylbenzoic acid from 2-chloro-4-phenylbenzoic acid by the Ullmann reaction, ring closure to give 3-phenylxanthone, treatment with phenylmagnesium bromide to give 3,9-diphenylxanthenol, and finally reduction to the xanthene.

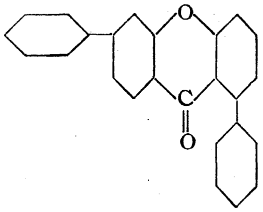
3,6,9-Triphenylxanthene was synthesized in a similar manner. 2-(3′-Phenylphenoxy)-4-phenylbenzoic acid (XIV) was obtained by the Ullmann reaction from potassium 2-chloro-4-phenylbenzoate and sodium-3-phenylphenolate. Ring closure gave two compounds, 3,6-diphenylxanthone (XV) and 1,6(or 3,8)-diphenylxanthone (XVI), of which only the one occurring in the larger amount was isolated in pure form. This compound was assigned the first structure (XV), inasmuch as ring closure of the acid should take place largely in the 6′-position since this position is para to the phenyl group and since the activity of the 2′-position should be decreased due to the blocking effect of the adjacent phenyl group. Moreover, the properties of the compound isolated were in agreement with the expectation that 3,6-diphenylxanthone would have a higher melting point and a lower solubility than the less symmetrical 1,6-diphenylxanthone. The final steps in the synthesis were the preparation of 3,6,9-triphenylxanthenol by treating 3,6-diphenylxanthone with phenylmagnesium bromide, and the reduction of the xanthenol to 3,6,9-triphenylxanthene (XIII).



XIV



XV



XVI

Experimental

9-Phenylxanthyl Chloride and Phenylmagnesium Bromide.—9-Phenylxanthyl chloride[11] was prepared by sus-

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[9] Unpublished results of J. Taras in this Laboratory.

[10] Scarborough and Waters, *J. Chem. Soc.*, 559 (1926); Bell, Kenyon and Robinson, *ibid.*, 1247 (1926).

[11] Gomberg and Cone, *Ann.*, **370**, 155 (1932).

pending 15 g. of the corresponding carbinol in 150 cc. of petroleum ether, adding 20 cc. of freshly distilled acetyl chloride and refluxing the mixture until all of the carbinol had dissolved. The solution was concentrated to about 75 cc. and the chloride allowed to crystallize. Moisture was excluded rigorously at all times. One recrystallization from petroleum ether gave pure colorless crystals of the chloride.

An ether solution of from 10 to 15 g. of 9-phenylxanthyl chloride was poured with swirling into an ether solution of twice the theoretical amount of phenylmagnesium bromide which was cooled in ice. Several minutes were required for the addition. At first, the Grignard solution in the vicinity of each entering drop of the chloride solution acquired an orange color which immediately disappeared, but as the reaction proceeded the solution became dark green. The mixture was refluxed for an hour, cooled and decomposed with ice and ammonium chloride. The ether extract was washed, concentrated and the product steam distilled, after which the residue was dissolved in ether and the solution dried over calcium chloride.

When the ether solution of the reaction product was allowed to evaporate spontaneously and slowly, a mass of white solid material formed which was found to be a mixture of 3,9-diphenylxanthene and 3,6,9-triphenylxanthene. The solid was filtered and washed with small amounts of cold ether, and the filtrate allowed further to evaporate very slowly. A second lot of white material was thus formed which was again composed chiefly of the above-mentioned compounds but which in some cases also contained very small amounts of 9,9-diphenylxanthene. No other substances could be isolated following this particular procedure.

The solubilities of 3,9-diphenylxanthene and 3,6,9-triphenylxanthene are very similar, hence they are difficult to separate. If the mixture was dissolved in hot acetic acid, a mass of crystals formed on cooling. When these crystals were digested with hot alcohol, a beady precipitate remained in the bottom of the flask and a flocculent precipitate became suspended in the solution, the two being separated by decantation. The flocculent precipitate was impure 3,6,9-triphenylxanthene, which could be obtained pure by repeated crystallization from ether, benzene or butanol. The beady precipitate and the material which dissolved in the alcohol was impure 3,9-diphenylxanthene, which could be obtained pure by crystallization from benzene.

Experiments indicated that no other compounds were present in appreciable amounts. Therefore, a melting point curve of known mixtures of these two compounds was prepared and the melting point of the unknown mixture was taken as a guide in estimating the percentage composition. In four typical runs, the estimated yields of 3,9-diphenylxanthene and 3,6,9-triphenylxanthene, respectively, were as follows: 34%, 14%; 43%, 3%; 51%, 6%; 51%, 14%. As mentioned previously, the variations in yield are due to experimental difficulty in isolating the crystalline compounds.

Molecular distillation with a Hickman still[12] was used in an attempt to better the yields, and if possible to isolate other products from the reaction mixture. Molecular distillation at a temperature of about 125° gave a large amount of material, part of which sublimed to the top of the still and part of which distilled into the receiver. Crystallization of the sublimed material from alcohol gave well formed crystals melting at 140–141° which showed no lowering in melting point when mixed with authentic 9-phenylxanthene. The distillate in the receiver was found to be a mixture of 9-phenylxanthene and 3,9-diphenylxanthene, from which the latter could be obtained in pure state by repeated recrystallization from alcohol. 3,6,9-Triphenylxanthene could not be recovered in this manner since when the temperature of the still was raised to 150°, decomposition occurred as was evidenced by blackening of the residue and evolution of gas.

The amount of 9-phenylxanthene present in the reaction mixture was determined by removing it by sublimation at 0.001 mm. pressure and 100°. The molecular sublimation apparatus was patterned after the still described by Carothers.[13] The quantities obtained in three experiments were 21, 13 and 19%, respectively.

9-(*p*-Biphenyl)-xanthenol.—Xanthone was added to an ether solution of excess *p*-biphenylmagnesium bromide and the mixture refluxed overnight. After chilling in an ice–salt-bath, the precipitate was filtered and decomposed with ice and hydrochloric acid. The ether extract was filtered to remove a small amount of insoluble dibiphenyl, then concentrated and steam distilled, and the residue dissolved in benzene from which practically pure biphenylxanthenol crystallized. Recrystallized from ether, the compound melted at 178–179°; yield, 85%. The carbinol gives a deep red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.38; H, 5.23.

9-(*p*-Biphenyl)-xanthene.—One gram of 9-(*p*-biphenyl)-xanthenol and 10 g. of dry sodium formate were added to 30 cc. of anhydrous formic acid and the mixture refluxed for one hour. At first, a deep red color was obtained but this soon disappeared and the xanthene crystallized. After dilution with water, the product was filtered and dried. Recrystallization from benzene gave colorless crystals which melted at 206–207°; yield, 95%.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.78; H, 5.43. Found C, 89.65; H, 5.49.

3-Bromo-4-methylbiphenyl.—Forty-four grams of 2-bromo-4-aminotoluene hydrochloride was treated with 25 cc. of concentrated hydrochloric acid, the mixture cooled in an ice–salt-bath and 18 cc. of water added. When cold a saturated solution of 16 g. of sodium nitrite was added dropwise to the mechanically stirred solution. Following the procedure of Gomberg and Bachmann,[14] the solution of the diazonium chloride was poured into 150 cc. of pure benzene at 5°, and 25 cc. of 40% sodium hydroxide solution added drop by drop over two hours, keeping the temperature below 9°; nitrogen was evolved. The stirring was continued for two to three hours. The resulting mixtures from two such runs were combined, the benzene layer concentrated and the product steam distilled at a temperature of 170–190°. About eight liters of distillate were caught, extracted with ether and the extract concentrated.

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[12] Hickman and Sanford, *J. Phys. Chem.*, **34**, 643 (1930), Fig. 6.

[13] Carothers and Hill, THIS JOURNAL, **54**, 1557 (1932).

[14] Gomberg and Bachmann, *ibid.*, **46**, 2339 (1924); Gomberg and Pernert, *ibid.*, **48**, 1372 (1926).

Distillation at 2 mm. pressure gave a light yellow oil which boiled at 123–123.5° and melted at 9°; yield 30%.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.36. Found: Br, 32.18.

Various attempts to oxidize 3-bromo-4-methylbiphenyl to 2-bromo-4-phenylbenzoic acid gave unsatisfactory yields.

3-Chloro-4-nitrobiphenyl.—Nineteen grams of 3-chloro-4-nitroaniline was heated to 70° with 45 cc. of concentrated hydrochloric acid, cooled, and diazotized by introducing a concentrated solution of sodium nitrite below the surface of the acid. The diazonium chloride solution was poured into 75 cc. of benzene, and 45 cc. of 40% sodium hydroxide solution added dropwise to the vigorously stirred mixture. The benzene solution was concentrated and the product distilling at 160–180° at 2 mm. pressure was crystallized from alcohol. Yellowish needles were obtained, melting at 78.5–79.5°; yield, 20%.

Anal. Calcd. for $C_{12}H_8ClNO_2$: Cl, 15.15. Found: Cl, 14.97.

3-Chloro-4-aminobiphenyl.—A solution of 10 g. of hydrated stannous chloride in 10 cc. of concentrated hydrochloric acid was poured slowly into a solution of 2 g. of 3-chloro-4-nitrobiphenyl in 15 cc. of alcohol. Repeated crystallization of the amine from dilute alcohol gave a compound melting at 69–69.5°. A mixed melting point showed that this compound was identical with the compound which Scarborough and Waters[10] obtained by chlorinating acetyl-4-aminobiphenyl and hydrolyzing the product. The latter method was therefore used for the preparation of further amounts of this amine.

3-Chloro-4-cyanobiphenyl.—This compound was obtained from 3-chloro-4-aminobiphenyl by the Sandmeyer reaction. The cuprous cyanide solution (150 cc.) was prepared in the usual manner from 18 g. of sodium cyanide, and was covered with 100 cc. of benzene and cooled to 5°. Twenty-four grams of 3-chloro-4-aminobiphenyl hydrochloride was suspended in 15 cc. of concentrated hydrochloric acid plus a small amount of ice and diazotized with a concentrated solution of sodium nitrite. The excess acid was made neutral to congo red paper with sodium bicarbonate solution and then added slowly to the vigorously stirred cuprous cyanide solution. The products of several such runs were combined and the benzene layer separated and washed with sodium carbonate solution and with water. Distillation at 2 mm. pressure followed by crystallization from alcohol gave the pure cyanide melting at 101–101.5°; yield 30%.

Anal. Calcd. for $C_{13}H_8ClN$: Cl, 16.60. Found: Cl, 16.39.

2-Chloro-4-phenylbenzoic Acid.—Twenty grams of 3-chloro-4-cyanobiphenyl was dissolved in 240 cc. of alcohol and 75 g. of 40% sodium hydroxide solution, and refluxed about six hours. The solution was cooled, poured into a liter of water, filtered, and the acid precipitated with hydrochloric acid. Crystallization from alcohol after treatment with norite gave white needles melting at 166.5–167°; yield 90%.

Anal. Calcd. for $C_{13}H_9ClO_2$: Cl, 15.25. Found: Cl, 15.19.

2-Phenoxy-4-phenylbenzoic Acid.—The potassium salt of 2-chloro-4-phenylbenzoic acid was prepared by dissolving the equivalent weights of the acid and of potassium carbonate in water, filtering the solution and concentrating to dryness on the sand-bath. To 3.5 g. of the salt was added 3.0 g. of phenol and a solution of sodium methylate prepared from 0.4 g. of sodium and 40 cc. of methanol, and the mixture refluxed until all the salt had dissolved. About 0.1 g. of copper powder was added and the methanol removed by distillation, after which the flask was placed in an oil-bath and the temperature slowly raised to 150°. At this temperature the reaction takes place rapidly and the temperature of the melt may reach 165–170°. After a few minutes the melt was cooled and digested with about 20 cc. of cold 5% sodium hydroxide solution. The phenol and original acid are quite soluble while the sodium salt of 2-phenoxy-4-phenylbenzoic acid is practically insoluble even in 1% sodium hydroxide solution. If necessary, the sodium salt may be purified readily by recrystallization from water. The acid was obtained by adding hydrochloric acid to a water solution of the sodium salt. Crystallization from alcohol or benzene gave colorless leaflets or small plates which melted at 169.5–170°; yield 80%.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.59; H, 4.87. Found: C, 78.51; H, 4.99.

3-Phenylxanthone.—When ring closure of 2-phenoxy-4-phenylbenzoic acid was attempted using hot concentrated sulfuric acid as the agent, a very poor yield of the xanthone was obtained; most of the product was water soluble and had a high melting point, indicating that sulfonation had occurred. The following procedure proved to be more satisfactory. Three grams of 2-phenoxy-4-phenylbenzoic acid was dissolved in 35 cc. of dry benzene, 3 g. of phosphorus pentachloride was added and the mixture heated. The solution thus obtained was cooled, 4 g. of anhydrous aluminum chloride added, and the mixture refluxed until no more hydrogen chloride was evolved. After treatment with ice, the product was steam distilled and the residue crystallized from alcohol or petroleum ether. Colorless needles were obtained melting at 141–141.5°; yield 95%.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.45. Found: C, 83.50; H, 4.55.

3,9-Diphenylxanthenol.—A benzene solution of 3-phenylxanthone was added to an ether solution of excess phenylmagnesium bromide, the mixture refluxed for one hour and then decomposed with ice and ammonium chloride. The benzene–ether layer was concentrated, steam distilled and the residue dissolved in hot petroleum ether. Colorless crystals were obtained which upon recrystallization from benzene–petroleum ether melted at 128.5–129°; yield 90%. With concentrated sulfuric acid, the carbinol gives a light red color with yellow-green fluorescence.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.49; H, 5.24.

3,9-Diphenylxanthene.—This compound was obtained by the reduction of 3,9-diphenylxanthenol with formic acid following the procedure described for the preparation of 9-biphenylxanthene. Crystallization from alcohol or petroleum ether gave colorless needles which melted at 146.5–147°; yield 95%.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.78; H, 5.43. Found: C, 89.53; H, 5.43.

2-(3′-Phenylphenoxy)-4-phenylbenzoic Acid.—3-Nitrobiphenyl was prepared by coupling diazotized *m*-nitraniline with benzene in alkaline solution,[15] and was reduced to 3-aminobiphenyl which was diazotized and added to boiling 30% sulfuric acid[16] to give 3-hydroxybiphenyl.

Four grams of potassium 2-chloro-4-phenylbenzoate, 3 g. of 3-hydroxybiphenyl and a methanol solution of sodium methylate prepared from 0.35 g. of sodium were placed in a flask, sufficient methanol being used so that the contents dissolved on refluxing. About 0.1 g. of copper powder was then added and the methanol removed by distillation, after which the flask was placed in an oil-bath and the temperature gradually raised. The reaction takes place readily at 150° and when the temperature of the bath reached 180° the flask was removed and the contents dissolved in about two liters of water containing a few grams of potassium hydroxide, after which the solution was filtered and the 2-(3′-phenylphenoxy)-4-phenylbenzoic acid precipitated with hydrochloric acid. Recrystallization from benzene or alcohol gave small, colorless needles which melted at 186–187°; yield 50–60%.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.93; H, 4.95. Found: C, 81.52; H, 4.95.

3,6-Diphenylxanthone.—Ring closure of 2-(3′-phenylphenoxy)-4-phenylbenzoic acid was accomplished with phosphorus pentachloride and aluminum chloride following the procedure described for the preparation of 3-phenylxanthone. A quantitative yield of crude material was obtained which appeared to be a mixture of 3,6-diphenylxanthone and 1,6-diphenylxanthone. Crystallization of this mixture from 1:1 methanol–benzene gave about a 35% yield of colorless needles which melted at 193.5–194.5°. The reasons for believing this compound to be 3,6-diphenylxanthone have been stated previously. The isomeric 1,6-diphenylxanthone was not obtained in pure form.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.18; H, 4.63. Found: C, 85.56; H, 4.64.

3,6,9-Triphenylxanthenol.—3,6-Diphenylxanthone, dissolved in benzene, was added to an ether solution of excess phenylmagnesium bromide and the mixture refluxed for about an hour. The product was decomposed with ammonium chloride and ice, and the ether extract concentrated and steam distilled. Crystallization of the residue from benzene gave colorless crystals which decomposed at 238–239°; yield 90%. With concentrated sulfuric acid, the carbinol gives a light red color with yellow-green fluorescence.

Anal. Calcd. for $C_{31}H_{22}O_2$: C, 87.29; H, 5.20. Found: C, 86.90; H, 5.32.

3,6,9 - Triphenylxanthene.—3,6,9 - Triphenylxanthenol was reduced to 3,6,9-triphenylxanthene by formic acid using the procedure previously described. Crystallization from benzene–petroleum ether gave small colorless plates which decomposed at 220°; yield 95%.

Anal. Calcd. for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.24; H, 5.42.

Summary

The reaction between 9-phenylxanthyl chloride and phenylmagnesium bromide has been studied, and it has been found that the chloride reacts largely in a quinonoid form and only to a limited extent in the benzenoid form. A number of xanthene derivatives have been prepared and described.

ANN ARBOR, MICH. RECEIVED DECEMBER 21, 1936

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(15) Blakey and Scarborough, *J. Chem. Soc.*, 3000 (1927).

(16) Jacobsen and Loeb, *Ber.*, **36**, 4083 (1903).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Structure of Metal Ketyls. V. The Conductance Function

BY CHARLES BUSHNELL WOOSTER

I. Introduction

Previous papers in this series[1] have reported some studies of the chemical reactions of monosodium benzophenone in liquid ammonia solution. It has become increasingly evident that such solutions comprise a system of rather complex equilibria and that further progress on the problem of the structure of metal ketyls would be facilitated greatly by more accurate information regarding the nature and interrelations of these equilibria. It is the purpose of the present paper to show that the conductance of sodium benzophenone in liquid ammonia as measured by Kraus and Bien[2] may be described quantitatively by assuming the presence of the following equilibria

$$[(C_6H_5)_2CO]Na \rightleftharpoons [(C_6H_5)_2CO]^- + Na^+ \tag{1}$$

$$2[(C_6H_5)_2CO]Na \rightleftharpoons (C_6H_5)_2C(ONa)\text{—}C(ONa)(C_6H_5)_2 \tag{2}$$

$$(C_6H_5)_2C(ONa)\text{—}C(ONa)(C_6H_5)_2 \rightleftharpoons Na^+ + Na[(C_6H_5)_2CO]_2^- \tag{3a}$$

$$[(C_6H_5)_2CO]Na + [(C_6H_5)_2CO]^- \rightleftharpoons Na[(C_6H_5)_2CO]_2^- \tag{3b}$$

that is, simple ionization of the metal ketyl (1), association of the metal ketyl molecules (ion pairs) to the un-ionized pinacolate (2), and formation of

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(1) (a) Wooster, THIS JOURNAL, **51**, 1858 (1929); (b) Wooster, *ibid.*, **56**, 2436 (1934); (c) Wooster and Holland, *ibid.*, **56**, 2438 (1934); (d) Wooster and Dean, *ibid.*, **57**, 112 (1935).

(2) (a) Kraus and Bien, *ibid.*, **55**, 3609 (1933); (b) Bien, Dissertation, Brown University, 1932.

triple ions by primary ionization of the pinacolate (3a) or by reaction between simple metal ketyl anions and metal ketyl ion pairs (3b). Only three of these four equilibria are independent and for the purpose of mathematical convenience equilibrium 3b has been chosen in preference to 3a as the basis of analysis; the reasons for omitting equilibria involving doubly charged pinacolate anions are discussed in the fourth section of this paper.

Kraus and Bien found that the conductance curve did not correspond to a simple binary equilibrium (as, for instance, that expressed in equation 1), and also noted that the equivalent conductance was much higher than that of the structurally similar salt, sodium benzohydrolate, at corresponding concentrations. They did not attempt further analysis of the conductance curve. According to the present interpretation the higher conductance may be attributed[3] in part to the presence of the third ionic species (triple ions) formed in accordance with equation 3b. This triple ion equilibrium bears a formal resemblance to that discussed by Fuoss and Kraus[4] but is distinctly different in two important respects. First, the triple ion formation is in the present instance due primarily to the quantum forces involved in the formation of a carbon–carbon bond. It is this fact which permits these triple ions to play an important part in the conduction process at concentrations between 0.01 and 0.0001 N in liquid ammonia where the formation of triple ions as the result of coulomb forces alone is excluded by the high dielectric constant of the medium. Second, these quantum forces operate only between the ion pair and an *anion;* there is no corresponding tendency toward triple ion formation by combination of an ion pair with a cation. As a result of this unilateral triple ion formation, the conductance function differs from that deduced by Fuoss and Kraus[4] for bilateral triple ion formation.

In Section II the conductance function for unilateral triple ion formation is derived and compared with the experimental results in the region 0.001–0.0001 N where the influence of the equilibrium expressed in equation 2 is negligible. In Section III the association of the ion pairs is considered and in Section IV the bearing of the results on the problem of the structure of the metal ketyls is discussed.

II. Unilateral Triple Ion Formation

For simplicity and for convenient comparison with the equations of Fuoss and Kraus we shall first consider the case of very low ion concentrations, where the activity coefficients and (square root) mobility corrections may be set equal to unity, and where the fraction of solute present as ions may be neglected in comparison with unity.

Abbreviating the simple ions as A^+ and B^- and representing the complex species in a corresponding manner, the mass action equation for the binary equilibrium

$$[A^+][B^-]/[AB] = K \qquad (4)$$

then reduces to

$$C\gamma(\gamma + \gamma_3) = K \qquad (5)$$

where C is the total concentration, K is the mass action constant, and γ and γ_3 are the ratios of the concentrations of the simple anions and the triple anions, respectively, to the stoichiometric concentration.[5]

The mass action equation for the triple ion formation

$$[AB][B^-]/[AB_2^-] = k \qquad (6)$$

reduces to

$$C\gamma/\gamma_3 = k, \ \gamma_3 = C\gamma/k \qquad (7)$$

and the observed conductance Λ is given by

$$\Lambda = \gamma\Lambda_0 + \gamma_3\lambda_0 \qquad (8)$$

where Λ_0 is the sum of the limiting conductances of the two simple ions, and λ_0 the sum of the limiting conductances of the triple ions and of the simple cations.

Solving equations 5 and 7 for γ and γ_3, substituting in equation 8 and simplifying gives

$$\Lambda(1 + C/k)^{1/2} = (\Lambda_0\sqrt{K})/\sqrt{C} + (\lambda_0\sqrt{K}/k)\sqrt{C} \qquad (9)$$

which differs from the corresponding equation of Fuoss and Kraus[6] by the coefficient of Λ. This coefficient prevents the equation from assuming a linear form on multiplication by $\sqrt{C}$, but a linear equation may be obtained from equation 9 in the following way. If we multiply equation 9 by $\sqrt{C}$, add and subtract $(C\Lambda_0\sqrt{K}/k)$ on the right-hand side of the equation, divide by $(1 + C/k)^{1/2}$, square both sides and simplify, we obtain

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[3] This interpretation supersedes the suggestion made in the previous paper, ref. 1d. However, it is possible that a part of this higher conductance may be due to a resonance phenomenon (discussed in the latter part of this paper) and therefore to this extent it may be the result of a certain analogy between sodium benzophenone and sodium triphenylmethyl.

[4] Fuoss and Kraus, This Journal, **55**, 2387 (1933).

[5] If C represents the total concentration in equivalents (as AB) per liter and the quantities in brackets represent concentrations of the included species, then $[B^-] = C\gamma$, $[AB_2^-] = C\gamma_3$, $[A^+] = C(\gamma + \gamma_3)$ and $[AB] = C(1 - \gamma - 2\gamma_3)$. In the simplified expressions above $(1 - \gamma - 2\gamma_3)$ is set equal to unity.

[6] Ref. 4, equation 4.

$$C\Lambda^2 = \Lambda_0^2K + [2\lambda_0/\Lambda_0 - 1 + (1 - \lambda_0/\Lambda_0)^2/(1 + k/C)]\Lambda_0^2KC/k \qquad (10)$$

The term $(1 - \lambda_0/\Lambda_0)^2/(1 + k/C)$ becomes negligible at sufficiently low concentrations and at high concentrations approaches asymptotically the limit $(1 - \lambda_0/\Lambda_0)^2$. Accordingly, this entire term may be neglected when the value of λ_0/Λ_0 is sufficiently close to unity to render $(1 - \lambda_0/\Lambda_0)^2$ negligible with respect to $(2\lambda_0/\Lambda_0 - 1)$. Under these conditions equation 10 assumes the following form which is linear with respect to the variables $C\Lambda^2$ and C.

$$C\Lambda^2 = \Lambda_0^2K + C(2\Lambda_0\lambda_0 - \Lambda_0^2)K/k \qquad (11)$$

This equation is, of course, applicable only to instances of unilateral triple ion formation at low total ion concentrations as for instance in dilute solution in a solvent of low dielectric constant. In order to apply it to solutions in solvents of higher dielectric constant such as liquid ammonia it is necessary to include the interionic terms in $\sqrt{C}$ in activity and mobility as well as the fraction of un-ionized solute which may no longer be set equal to unity. These corrections may be approximated in the manner of Fuoss and Kraus[4] by substituting $2C\Lambda/\Lambda_0$ for the ion concentration $2C(\gamma + \gamma_3)$ in the usual formulas and applying the results as appropriate correction terms to (11).

If the various corrections are made to (5), (7) and (8), by introducing the activity coefficient f defined by the relation $-\log f = \beta\Lambda_0^{-1/2}\sqrt{C\Lambda}$, a mobility coefficient $m = 1 - \alpha\Lambda_0^{-3/2}\sqrt{C\Lambda}$ and the term $(1 - \Lambda/\Lambda_0)$ as an approximation for the un-ionized fraction of the solute, we obtain

$$\begin{aligned} &Cf^2\gamma(\gamma + \gamma_3)/(1 - \Lambda/\Lambda_0) = K \\ &C\gamma(1 - \Lambda/\Lambda_0)/\gamma_3 = k \\ &\gamma_3 = C\gamma(1 - \Lambda/\Lambda_0)/k, \text{ and} \\ &\Lambda = m(\gamma\Lambda_0 + \gamma_3\lambda_0) \end{aligned}$$

Combining these equations[7] yields the corrected form of equation 11

$$\left(\frac{f\Lambda}{m}\right)^2 \frac{C}{(1 - \Lambda/\Lambda_0)} = \Lambda_0^2K + \frac{(2\Lambda_0\lambda_0 - \Lambda_0^2)K}{k}\left(1 - \frac{\Lambda}{\Lambda_0}\right)C \qquad (12)$$

Comparison with Experiment.—In order to apply equation 12 to the conductance data on monosodium benzophenone, it is necessary to choose a value for Λ_0. As a matter of fact, the linearity of the equation is not very sensitive to the value of Λ_0 chosen, which therefore need only be approximate. In consequence, however, equation 12 is of little assistance in suggesting a choice of Λ_0. Fortunately this constant may be closely approximated from a knowledge of the conductance of similar salts in liquid ammonia. The limiting equivalent conductance of the sodium ion in liquid ammonia[8] is known to be 130 and the limiting equivalent conductances, Λ_0', of a number of anions in liquid ammonia[8] are collected in Table I.

TABLE I

CONSTANTS OF ELECTROLYTES IN AMMONIA

No.	Salt	Λ_0	Λ_0'	$K \times 10^4$	$a \times 10^8$
1	KNH_2	351	187	0.7	2.2
2	$NaNHC_6H_5$	316	(186)	8.2	3.1
3	$NaOC_6H_5$	279.4	149.3	3.82	2.7
4	$NaN(C_6H_5)_2$	235	105	58	6.7
5	$KN(C_6H_5)_2$	266	102	50.5	6.0
6	$NaSn(C_6H_5)_3$	226	96	130	(10.4)
7	$KNH_2 \cdot B(C_6H_5)_3$	257	93	130	10.4
8	$NaNH_2 \cdot B(C_6H_5)_3$	215	85	150	10.9

Since the values of Λ_0' in a given solvent at a fixed temperature are doubtless primarily determined by the size of the migrating ion, the value of Λ_0' for the ion $[(C_6H_5)_2CO]^-$ may be expected to lie between the limits 96 and 105 and to be closer to the upper than to the lower limit. For purposes of calculation the upper value has been chosen so that $\Lambda_0 = 235$. The value of λ_0' may be estimated from the assumed value of Λ_0 by means of Stokes's law to be approximately 77, corresponding to $\lambda_0 = 207$. On this basis, the maximum alteration in the slope of the plot due to the neglected term of equation 10 would be 1.87%, which is well within the limits of experimental error.

A plot of $f^2C\Lambda^2/m^2(1 - \Lambda/\Lambda_0)$ against $C(1 - \Lambda/\Lambda_0)$ appears in Fig. 1 and, in conformity with the requirements of equation 12, this plot is linear throughout the dilution range 10^3–10^4 liters. The values of the constants obtained from the intercept and slope are, respectively, $\Lambda_0^2K = 5.6$ and $(2\Lambda_0\lambda_0 - \Lambda_0^2)K/k = 2.4 \times 10^3$. Introducing the estimated values of Λ_0 and λ_0, the following values are obtained for the mass action constants: $K = 1.01 \times 10^{-4}$ and $k = 1.8 \times 10^{-3}$.

III. The Association of Ion Pairs

At concentrations above 0.001 N the equivalent conductance of monosodium benzophenone falls below that predicted by equation 12. This deviation may be due in part to the failure at higher ion concentrations of the approximations intro-

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[7] The coefficients α and β have the same significance as in the paper of Fuoss and Kraus [THIS JOURNAL, **55**, 476 (1933)]. In liquid ammonia at its boiling point $\alpha = 2.133\Lambda_0 + 442$ and $\beta = 4.742$.

[8] Fuoss and Kraus, *ibid.*, **55**, 1027 (1933); Kraus and Hawes, *ibid.*, **55**, 2784 (1933); Kraus and Kahler, *ibid.*, **55**, 3541 (1933); Kraus and Johnson, *ibid.*, **55**, 3545 (1933).

duced in the estimate of the activity and mobility terms, etc. However, these deviations seem to be much larger than would be expected on this basis alone and it is likely that they are due primarily to a reduction in the concentration of the ion pairs as the result of association in accordance with equation 2.

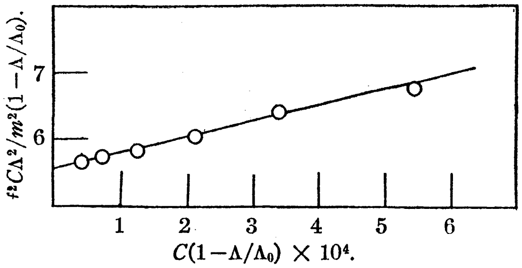

Fig. 1.—Unilateral triple ion formation.

Equation 12 may be corrected for this effect by introducing the term $C\gamma_2(1 - \Lambda/\Lambda_0)$ in place of $C(1 - \Lambda/\Lambda_0)$ for the concentration of the ion pairs, (γ_2 represents the fraction of non-conducting solute present as ion pairs) and assumes the form

$$\left(\frac{f\Lambda}{m}\right)^2 \frac{C}{(1-\Lambda/\Lambda_0)\gamma_2} = \Lambda_0^2K + \frac{(2\Lambda_0\lambda_0 - \Lambda_0^2)K}{k}\left(1-\frac{\Lambda}{\Lambda_0}\right)C\gamma_2 \qquad (13)$$

The mass action equation for ion pair association

$$[AB]^2/[A_2B_2] = k_4 \qquad (14)$$

reduces to

$$2C\gamma_2^2(1-\Lambda/\Lambda_0)/(1-\gamma_2) = k_4 \qquad (15)$$

and the required values of γ_2 could be obtained if k_4 were known. Conversely k_4 should be determined by the values of γ_2 required to satisfy equation 13. These may be obtained from the experimental results by substituting the constants as determined at lower concentrations in equation 13 and solving for γ_2. Since equation 15 may be transformed as follows

$$2C\gamma_2(1-\Lambda/_0) = k_4/\gamma_2 - k_4 \qquad (16)$$

the values of γ_2 may be tested for conformity with the mass action equation by plotting $2C\gamma_2(1 - \Lambda/\Lambda_0)$ against $1/\gamma_2$. The plot should yield a straight line crossing the $1/\gamma_2$ axis at unity and k_4 may be obtained from either the slope or the other intercept. Such a plot appears in Fig. 2 from which it is evident that the values of γ_2 comply satisfactorily with the stated requirements over the dilution range 50–800 liters, yielding the value $k_4 = 1.56 \times 10^{-2}$.

Calculation of the Conductance Curve.—The conductance curve may be calculated from the final conductance equation (13) in the following way. Abbreviating $C(1 - \Lambda/\Lambda_0)$ to x and substituting the values of the constants, equation 13 may be solved readily for $f C\Lambda/m$

$$fC\Lambda/m = \sqrt{5.6x\gamma_2 + 2400(x\gamma_2)^2} \qquad (17)$$

and, similarly, equation 15 may be solved for γ_2

$$10^2\gamma_2 = -0.39/x + \sqrt{(0.39/x)^2 + 78/x} \qquad (18)$$

Thus by substituting arbitrary values of x, the corresponding values of $fC\Lambda/m$ may be obtained from equations 18 and 17. Since $fC\Lambda/m$ is a function of $C\Lambda$ and known constants (Λ_0, β and α), the corresponding values of $C\Lambda$ may be read from a plot of $fC\Lambda/m$ against $C\Lambda$. The concentration corresponding to the chosen value of x is then given by $C = x + C\Lambda/\Lambda_0$ and Λ may be obtained from C and $C\Lambda$. Of course, for sufficiently low values of x it is possible to set $\gamma_2 = 1$ and dispense with the use of equation 18.

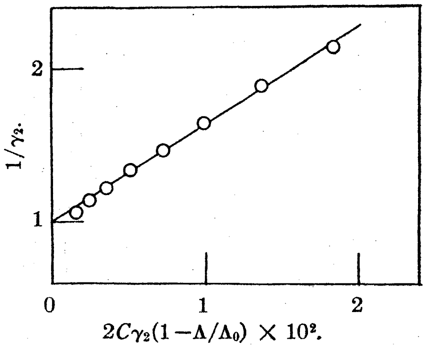

Fig. 2.—Ion pair association.

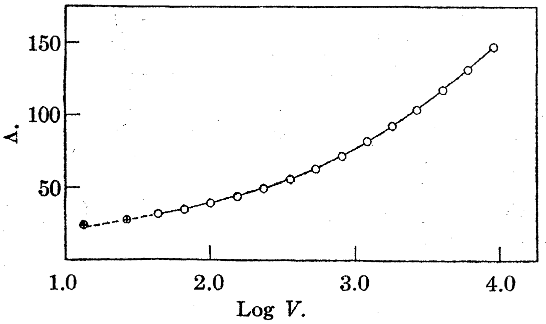

Fig. 3.—The conductance curve.

In Fig. 3 a plot of Λ against log V is shown in which the calculated values are represented by the continuous curve and the experimental values by the circles. In addition to the published values, Kraus and Bien obtained two series of lesser accuracy. These measurements show erratic deviations at high dilutions, but at higher concentrations, where they are more reliable, the two series agree with the calculated curve within the limits of experimental error. Two measurements from one of these series, which were made at higher concentrations than any of the published values, are indicated in Fig. 3 by the crossed circles and lie reasonably close to the calculated curve. The extrapolated portion of this curve is represented in the figure by a broken line.

IV. Discussion of Results

There can be no doubt that the final conductance equation adequately reproduces the experimental data and there is no reason to question the existence of the postulated equilibria involving the five solute species: AB, A_2B_2, A^+, AB_2^-, B^-. The existence of the simple ions and the corresponding ion pairs is indicated by all the well-known evidence in favor of the free radical nature of the metal ketyls, and association to the pinacolate (A_2B_2 or its ions) has been demonstrated both in ether[9] and in liquid ammonia solution.[1b] The omission of the sixth solute species (B_2^{--}, the doubly charged pinacolate anion) in the formulation of the conductance equation was based on the assumption that this ion would be too highly dissociated (in virtue of the electrostatic repulsion of the two negative charges) to play a significant part in the conduction process. Although there is no entirely independent evidence in support of this assumption, it is interesting to note that the assumption may be shown to be consistent with the observed values of the mass action constants.

The primary ionization constant of the pinacolate, K_4, may be calculated from the other three constants

$$[A^+][AB_2^{--}]/[A_2B_2] = K_4 = Kk_4/k = 8.75 \times 10^{-4}$$

and from this value the corresponding secondary ionization constant, $K_3 = [A^+]\,[B_2^{--}]/[AB_2^-]$, may be estimated roughly to be 5.23×10^{-7} by suitable modifications of the method of Fuoss and Kraus.[10] Since the concentration of sodium ions cannot be less than that of the triple anions ($[A^+] > [AB_2^-]$), the concentration of pinacolate anions, $[B^{--}]$, cannot exceed 5.23×10^{-7}. The ratio of the concentration of the pinacolate anions to that of the simple anions is proportional to the square root of the former

$$[B_2^{--}]/[B^-] = (K_3[B_2^{--}]/kK)^{1/2} = 1.7[B_2^{--}]^{1/2}$$

and on substituting 5.23×10^{-7} as the maximum value of $[B_2^{--}]$, the maximum value of the ratio is found to be 1.23×10^{-3}, which implies that only a negligible fraction of the current is carried by the doubly charged pinacolate anions at any concentration.

For these reasons we may proceed to discuss the significance of the results with respect to the structural problems of the metal ketyls on the assumption that the observed mass action constants represent the true values within the limits of error imposed by the approximations introduced in the correction terms for mobility, activity and un-ionized fraction.

The Structure of the Ion Pair.—Previous studies of the reaction between the metal ketyl and alkyl halides[1] have furnished evidence that the observed carbon alkylation occurs in the first step of the reaction, presumably as the result of a simple substitution process. On this basis, the suggestion was made that the charge on the metal ketyl anion was not located exclusively on the oxygen atom, but was "shared" to some extent with the extra-nuclear carbon. The available chemical evidence does not permit a precise definition of the term "shared"; this evidence is equally compatible with a model involving a triple electron bond between carbon and oxygen and with a resonance model,[11] including in the complete wave equation the structures $(C_6H_5)_2\underset{\cdot}{C}:\underset{\cdot\cdot}{\ddot{O}}:$ and $(C_6H_5)_2\underset{\cdot\cdot}{C}:\underset{\cdot}{\ddot{O}}:$ together with many others which locate the charge on quinonoid rings. Furthermore, the extent to which a similar sharing is involved in the structure of the ion pair is not revealed by the chemical evidence, for it is even conceivable that the ion pairs undergo alkylation only after a preliminary separation into free ions.[12]

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[9] Bachmann, THIS JOURNAL, **55**, 1179 (1933).

[10] Fuoss and Kraus, *ibid.*, **55**, 1021–1024 (1933). When one ion is doubly charged, equation 6 of Fuoss and Kraus assumes the form

$$K_3^{-1} = \frac{4\pi N}{1000}\left(\frac{2e^2}{DkT}\right)^3 Q(b)$$

where $Q(b)$ is the function tabulated by these authors and $b = 2e^2/aDkT$. In making the above estimate, the fact that the two charges in the pinacolate anion are not located at the same point was ignored. This corresponds very crudely to the assumption that the sodium ion is equidistant from the two negative charges in the triple ion. The value used for the parameter a was that corresponding to the primary ionization constant, K_4. Since K_4 is greater than K, it is possible that repulsion between the sodium ions in the pinacolate may play a part in determining K_4. Such repulsion is absent in the triple ion and *on this basis* it would be predicted that the parameter a corresponding to K_3 should be less than that assumed and, accordingly, the estimated value of K_3 might be regarded as a maximum.

[11] (a) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933); (b) Bent and Keevil, *ibid.*, **58**, 1370 (1936).

[12] It is, perhaps, desirable to state here that the phrase "carbon–sodium bond in the metal ketyl" used in the previous paper of this series (ref. 1d) was not intended to refer specifically to the ion pair. In fact, it was immediately elaborated in terms of the free anion. It was used as a general term to designate a structural fea-

Fuoss and Kraus[10] have derived an expression relating the dissociation constant of an ion pair to a parameter *a* which may be considered as the minimum distance of separation of the positive and negative charges in an ion pair formed from spherical ions. Although the significance of *a* cannot be so simple when unsymmetrical ions are involved, it seems reasonable to suppose that even in such cases *a* is primarily determined by this minimum distance.[13] Accordingly it is interesting to compare the *a* value for the metal ketyl ion pair with the estimates of those corresponding to the ionization of sodium benzohydrolate, $(C_6H_5)_2CHONa$, and the primary ionization of disodium benzophenone, $(C_6H_5)_2CNaONa$, which appear in Table II.[14]

TABLE II

CONSTANTS OF SODIUM BENZOPHENONE AND RELATED SALTS IN LIQUID AMMONIA

No.	Salt	$K \times 10^4$	$a \times 10^8$
1	$[(C_6H_5)_2CHO]Na$	0.32	2.01
2	$[(C_6H_5)_2CO]Na$	1.01	2.28
3	$[(C_6H_5)_2CONa]Na$	3.2	2.70

In the sodium benzohydrolate ion pair the sodium ion is presumably located in the vicinity of the oxygen atom which carries the anionic charge. The *a* value for this salt, lower than any listed in Table I, is entirely compatible with this model, for it indicates the absence of the steric factors which, coming into play on closer approach of the sodium ion to the phenyl groups, result in the much larger *a* value of sodium diphenylamide. The very low *a* value is probably also due in part to specific influences resulting from the location of the charge on oxygen, as is suggested by comparison of the *a* values for the similarly constituted sodium phenolate and sodium anilide (nos. 3 and 2, Table I).

The primary ionization of disodium benzophenone is in some respects the closest available analog of the ionization of a metal ketyl ion pair in which the charge is effectively located on the extra-nuclear carbon, but it is probable that the *a* value is somewhat lower than that which would correspond to the ionization of such a metal ketyl ion pair.[15] Nevertheless, the fact that the observed *a* value for the actual metal ketyl ion pair lies between the other two listed in Table II is qualitatively significant and may be interpreted in two ways. First, the actual structure of the metal ketyl ion pair may not correspond to a model in which the sodium ion is definitely located in the vicinity of the oxygen (*i. e.*, analogous to sodium benzohydrolate) or to one in which the sodium ion is located in the vicinity of the extra-nuclear carbon, but it may, instead, possess an intermediate character. If the *a* values are assigned quantitative significance, the intermediate structure would appear to be approximated more closely by the first model. Second, the structure of the metal ketyl anion may correspond to the resonance model, previously mentioned, and the sodium ion may be definitely located in the vicinity of the oxygen in the ion pair. On this basis, the increase in the *a* value over that of sodium benzohydrolate can be ascribed to the coulomb interaction of the sodium ion and the electrons which may be considered to give rise to resonance in the

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ture which might characterize either the ion pair, the free anion or both. From this point of view, it is evident that the conclusions of Bent (ref. 11b) regarding the structure of the ion pair are restrictive rather than contradictory. Further discussion regarding the relation between the chemical evidence and the structure of the ketyl anion will be reserved for a subsequent paper.

(13) As calculated from dissociation constants by Coulomb's law, the parameter *a* gives the diameter of a fictitious sphere which will duplicate the properties of the real physical system. Since a strictly accurate calculation should involve a form factor, the omission of this factor in the present theory is absorbed in the numerical value of *a*. Consequently, any space factor (steric hindrance) which would decrease the probability of formation of ion pairs will appear as a numerically larger *a* value than that corresponding to the actual atoms on which the charges are located.

(14) The data on the conductance of sodium benzohydrolate in liquid ammonia[2] are not sufficiently accurate to permit the precise determination of Λ_0 by extrapolation. By the use of the approximate formula

$$K = \left(\frac{f\Lambda}{m\Lambda_0}\right)^2 \frac{C}{(1 - \Lambda/m\Lambda_0)}$$

setting $\Lambda_0 = 235$, the value of $K \times 10^4$ for this salt was found to lie between 0.29 and 0.35 over the dilution range 616–6450 liters per mole. The average of ten determinations from two independent series of measurements was 0.32. The data on disodium benzophenone were treated in a similar way, attributing all of the conductance to the primary ionization (in order to obtain a maximum value of K for this process) and setting $\Lambda_0 = 221$ (estimated for $[Na^+][(C_6H_5)_2CONa]^-$ by means of Stokes' law). The resulting values of $K \times 10^4$ fell between the limits 2.8 and 3.7 over the dilution range 96–1700 liters per mole and the average of nine determinations from two independent series was 3.2.

(15) Two disturbing factors which are absent in such a metal ketyl ion pair may play a significant part in the determination of the *a* value found for disodium benzophenone. The fact that this primary dissociation may lead to the formation of two types of anions might be expected to result in greater ionization and accordingly to a somewhat larger *a* value than would otherwise be the case. On the other hand, it seems likely that in any reasonable models of un-ionized disodium benzophenone which locate one sodium ion in the vicinity of the extra-nuclear carbon and the other in the vicinity of the oxygen, the first sodium ion will be closer to the negatively charged oxygen than to the other sodium ion. Accordingly, the resultant influence of the sodium–oxygen dipole on the first sodium ion will be an attraction and will tend to reduce the ionization and the corresponding *a* value. Since this effect is fundamentally similar to that responsible for bilateral triple ion formation which does not occur extensively except in solvents of much lower dielectric constant, it would be expected to reduce the *a* value by only a moderate amount, yet it appears to counteract both the first disturbing influence mentioned above as well as at least a part of the steric hindrance of the phenyl groups.

metal ketyl anion as a result of their wandering around in the benzene rings.[11b] This coulomb interaction would tend to localize the charge electron in the vicinity of the sodium ion so that the ion pair would be formed at the expense of some of the resonance energy of the anion, and the resulting instability of the ion pair would be revealed by an increase in the values of K and a. The difference between the a values of the metal ketyl and of sodium benzohydrolate corresponds to an energy difference of 0.55 kcal., which could be considered as an approximate measure of the *minimum*[16] contribution of the charge electron to the resonance energy of the free anion. The conductance data furnish no basis for a decision between these two interpretations, but the evidence advanced by Bent[11b] establishes a presumption in favor of the second hypothesis. It should be noted, however, that these alternative hypotheses are merely limiting cases since the two factors suggested as possible causes of the increased a value are not, necessarily, mutually exclusive.

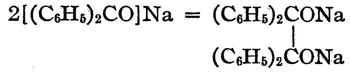
The Association of Ion Pairs.—The mass action constants k and k_4 are much more sensitive than K to errors[17] in the approximations introduced in applying the conductance equation and are, perhaps, reliable only as to order of magnitude. The independent evidence regarding association to the pinacolate in 0.3 normal solution, presented in the second paper of this series,[1b] indicated a much lower degree of association than is obtained by extrapolation to that concentration using these observed values of the mass action constants. Although such extrapolation is justified only as a crude approximation, it is unlikely that the discrepancy is due entirely to the uncertainties in the constants or in the extrapolation. It is probable that the actual proportion of pinacolate in such concentrated solutions is higher than was indicated by the application of a modification of Bachmann's method[9] to liquid ammonia solutions, and that a considerable fraction of the pinacolate dissociated during the decomposition with ammonium chloride.

Summary

1. It has been shown that the conductance of sodium benzophenone in liquid ammonia may be described quantitatively by assuming the presence of the following equilibria

$$[(C_6H_5)_2CO]Na = [(C_6H_5)_2CO]^- + Na^+$$

$$[(C_6H_5)_2CO]Na + [(C_6H_5)_2CO]^- = Na[(C_6H_5)_2CO]_2^-$$



$$2[(C_6H_5)_2CO]Na = \begin{array}{c}(C_6H_5)_2CONa \\ | \\ (C_6H_5)_2CONa\end{array}$$

2. The structure of the ion pair has been discussed. The available evidence is consistent with the hypothesis that the sodium ion is located in the vicinity of the oxygen in the ion pair, provided it is further assumed that this ion pair is formed at the expense of some of the resonance energy of the free anion and that the charge electron participates in the resonance phenomenon in this anion.

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[16] The coulomb interaction may cancel only a fraction of the contribution of the charge electron to the resonance energy.

[17] It seems likely that such errors can be reduced by using a solvent of lower dielectric constant. Accordingly, an attempt will be made to measure the conductance of metal ketyls in pyridine.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Dissociation Constants of Diaquotetrammine Cobaltic Cation as an Acid

BY ARTHUR B. LAMB AND EDWIN B. DAMON

Diaquotetrammine cobaltic ion may be regarded, in accordance with Brønsted's definition, as a cation acid which dissociates in two steps as follows

$$[Co(NH_3)_4(H_2O)_2]^{+++} \longrightarrow [Co(NH_3)_4(H_2O)(OH)]^{++} + H^+$$

and

$$[Co(NH_3)_4(H_2O)(OH)]^{++} \longrightarrow [Co(NH_3)_4(OH)_2]^+ + H^+$$

Brønsted and his collaborators[1] have measured the primary dissociation constants of this and of a number of similar aquo ion acids and have found interesting differences among them. Their measurements, in the case of the diaquotetrammine cation, were carried out by two independent methods. In the first method, the solubility of the slightly soluble diaquotetrammine salt of the oxalodinitrodiammine cobaltic anion was measured in solutions of varying known acidity; this was compared with the solubility of the luteo salt under similar conditions. In the

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[1] J. N. Brønsted and C. V. King, *Z. physik. Chem.*, **130**, 699 (1927); J. N. Brønsted and K. Volqvartz, *ibid.*, **134**, 97 (1928).

second method, the concentration of hydrogen ion in a solution containing this cation was ascertained from the rate of aquation of added nitratoaquotetrammine cobaltic nitrate (as shown by measurements of the electrical conductance of the solution).

These methods are ingenious and elegant and have evidently been applied with skill. Nevertheless there appear to be difficulties inherent in them, since successive determinations by both methods under substantially identical conditions showed variations of 20% and more in the dissociation constants obtained.

In this situation it has seemed to us worth while to ascertain whether the glass electrode, thanks to its rapidity of response and its indifference to the presence of oxidizing substances, could not be used to measure these constants with greater precision and certainty. We have, therefore, applied this instrument to solutions of diaquotetrammine cobaltic chloride containing known, varying amounts of sodium hydroxide. In other words, we have carried out a non-cumulative electrometric titration of the cation acid.

This procedure has the advantage that minute impurities, which might seriously alter the hydrogen ion concentration if the salt were merely dissolved in pure water, have a decidedly smaller effect in the presence of the added alkali. Also, measurements in the more alkaline solutions permit the determination of the secondary as well as the primary disssociation constant.

From numerous points on the titration curve thus obtained, we have computed a series of values for the primary and also for the secondary dissociation constant of the diaquotetrammine ion.

In carrying out this titration it was important to recognize that this ammine is by no means a stable substance under these conditions. In the first place, it changes into the acido salt to at least a limited extent; Stevens[2] found in the case of the chloride that in a 0.005 M solution at 25° an equilibrium was reached in about 200 minutes, at which analyses indicated the presence of 12% of the chloroaquoammine. In the second place, this ammine suffers an irreversible decomposition in which ammonia is liberated and an oxide or hydroxide of cobalt ultimately is precipitated. While in acid solution this decomposition is relatively slow, the rate increases rapidly as the solution becomes more alkaline and this decomposition sets an upper limit to the pH value at which useful measurements can be made.

Apparatus

The glass electrode assembly used in these measurements was of the convenient, durable type described by MacInnes and Belcher.[3]

Measurements of e. m. f. were made with a Compton quadrant electrometer and a Leeds and Northrup type K potentiometer, standardized against an Eppley standard cadmium cell. With this arrangement it proved more rapid and convenient not to balance the potentiometer exactly, but rather to set the slide wire within one or two millivolts of the unknown e. m. f., and then determine the difference from the electrometer deflection. The total deflection on reversing the connections to the electrometer amounted to not less than 10 mm. per millivolt, so that the e. m. f. could be measured to 0.1 mv.

For this use with an electrometer the series of tapping keys provided in the potentiometer for use with a galvanometer were disconnected by detaching the movable part of the switch marked "STD. CELL–E.M.F.," leaving the center posts of the switch open. The end posts of the switch were then bridged across by U-shaped brass strips, which served to connect the "E.M.F.–" and the "STD CELL–" binding posts directly to the potentiometer circuit. An external switchboard could then be connected to the potentiometer through the "E.M.F." and "STD. CELL" binding posts, without making any internal changes.

The glass electrode assembly, potentiometer and auxiliary apparatus were surrounded by appropriate electrostatic shields of copper sheet or gauze, which were interconnected and earthed. The potentiometer and its accessories were kept dry by trays of calcium chloride, and were operated from outside the shield by means of suitably insulated, earthed metal rods.

The glass electrode and the solutions were contained in a large air thermostat which, undisturbed, maintained a temperature of 25.00 ± 0.02°. However, opening the door to operate the glass electrode caused fluctuations of temperature which were best corrected by a manual readjustment. Readings of the temperature made at the time of every measurement with the glass electrode showed, however, that the temperature of the cell could hardly have varied more than about 0.1° from 25.0° during these measurements.

Materials

Diaquotetrammine cobaltic chloride was prepared from pure carbonatotetrammine chloride (described below) by the method of Jörgensen.[4] The crystals thus obtained were washed 3–5 times with ice-cold concentrated hydrochloric acid, then 3–5 times with cold 95% alcohol, a motor-driven centrifuge being used to settle the wash liquors before decantation. They were then transferred to a platinum Gooch crucible, washed 5 times with absolute alcohol and drained in the centrifuge. After a final centrifuging

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(2) R. G. Stevens, Thesis, Harvard University, 1927.

(3) Duncan A. MacInnes and Donald Belcher, *Ind. Eng. Chem., Anal. Ed.*, **5**, 199 (1930).

(4) S. M. Jörgensen, *Z. anorg. Chem.*, **2**, 294 (1894).

for twenty to fifty minutes, the apparently dry crystals were exposed in the open air for one to two hours before weighing. The product was in all cases used on the day it was prepared.

Analyses of the six different preparations used in these measurements gave the following percentages of cobalt: 21.93, 21.93, 21.96, 21.92, 21.94, 21.96; average, 21.94. Analysis of a seventh sample, prepared in the same way, gave the following additional data.

	I	II	Average	Calculated for $Co(NH_3)_4(H_2O)_2Cl_3$
Cobalt, %	21.93	21.92	21.93	21.87
Total chlorine, %	39.39	39.40	39.39	39.47_5
Complexly bound chlorine, %	0.236	0.230	0.233	0.000

The high value found for cobalt probably indicates the presence of a small amount of cobalt oxide, formed by decomposition of the complex. The 0.233 g. of complexly bound chlorine found in 100 g. of sample is equivalent to 1.650 g. of chloroaquotetrammine chloride, containing 0.699 g. of chlorine all told. This leaves 38.69 g. of chlorine, equivalent to 98.02 g. of diaquotetrammine chloride, in 100 g. of sample. The cobalt analyses show an excess of cobalt over that contained in these ammines equivalent to 0.19 g. of cobaltic hydroxide. The analysis of this sample thus corresponds to that of such a mixture as

Diaquotetrammine chloride	98.02%
Chloroaquotetrammine chloride	1.65%
Cobalt hydroxide, $Co(OH)_3$	0.19%
Moisture, etc., by difference	0.14%

Previous investigators who have analyzed this salt have obtained low values for chlorine and high values for cobalt. Thus for total chlorine Jörgensen[4] found 39.17 *versus* 39.475%, and for cobalt Birk[5] found 21.95 *versus* 21.87%.

Carbonatotetrammine Cobaltic Chloride.—This ammine prepared by following the directions of Jörgensen[6] proved on analysis to have a low and variable content of chlorine. This presumably was caused by the presence therein of carbonato bicarbonate and by the separation of a part of the product as an oil, rather than as crystals, on precipitation with alcohol.

We found that these difficulties could be remedied by a more careful regulation of the concentration of ammonium carbonate and ammonium chloride, and, after careful precipitation with alcohol, by recrystallizing the product first from a solution of ammonium chloride and finally from water. Our procedure with these supplementary details was as follows.

Twenty grams of cobalt carbonate was dissolved, with warming, in 56 ml. of 1:1 hydrochloric acid. The clear solution, diluted to 100 ml., was poured into 800 ml. of a solution containing 100 g. of ammonium carbonate and 250 ml. of concentrated ammonium hydroxide (sp. gr., 0.90). After oxidation by a vigorous current of air for three hours, the solution was transferred to a porcelain dish (diameter, 30 cm.) and evaporated on a steam-bath for two hours, with the addition of small (2.5 to 3 g.) lumps of ammonium carbonate at five-minute intervals. The solution, now concentrated to a volume not greater than 250 ml., was filtered while warm, cooled in an ice-bath and diluted to 300 ml. with a solution containing 18 g. of ammonium chloride in the required amount of distilled water. The solution, cooled in ice, was treated with 750 ml. of cold 95% alcohol, added in 50-ml. portions at ten-minute intervals. The product, which usually separated in good crystalline form, was collected on a suction filter, washed with cold 70% alcohol and dried in the open air; yield, about 24 g.

The crude material from ten such batches was combined for purification. To convert into chloride any carbonato bicarbonate that might be present, it was dissolved at room temperature in the required amount of a 15% solution of ammonium chloride, which had been made neutral to litmus with ammonium hydroxide; the resulting solution was cooled in ice and treated with cold 95% alcohol added in 150-ml. portions at ten-minute intervals. The crystals thus formed were collected and washed as before.

After two such recrystallizations, the product was crystallized once from water without the addition of alcohol. In this process, the salt was divided in several portions, and the mother liquor from the crystallization of the first portion used over and over again. (At the end, a small amount of less pure material was precipitated by adding alcohol to the mother liquor.) The crystals were collected in a platinum Gooch crucible, washed once with cold water and drained in the centrifuge; yield, 101 g. of good crystals, plus 18 g. of less pure material.

The crystals obtained in this way were clear, garnet-red 4- and 6-sided prisms, mostly small, but a few as long as 1 mm. On standing, the crystals became less transparent, while the color changed toward purple. After being ground and exposed over calcium chloride for forty-eight hours they were analyzed with the following results.

	I	II	Average	Calculated for $Co(NH_3)_4(CO_3)Cl$
Cobalt, %	26.56	26.54	26.55	26.49
Chlorine, %	15.94	15.91	15.92_5	15.93

Standard Solution of Sodium Hydroxide, 0.1 M.—A solution sufficiently free from carbonate for our purposes was prepared by the method of Sørensen[7] and Cowles.[8] After dilution with boiled distilled water, the solution was standardized first against potassium biphthalate and found to be 0.0999, 0.1001 and 0.1001 *M;* and second, against oxalic acid and found to be 0.1001, 0.1001 and 0.1000 *M;* average, 0.1000_5 *M;* temperature, 23–24°. The solution was kept in a Pyrex bottle, protected by soda-lime tubes.

Analytical Methods

Cobalt was determined as usual by conversion to cobaltous sulfate. A porcelain crucible was employed with the serrated, clear quartz lid described by J. D. Main Smith[9] for prevention of loss by spattering.

In determining the complexly bound chlorine in the diaquotetrammine chloride (presumably present as chloroaquo chloride) every precaution was taken to prevent loss

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(5) E. Birk, *Z. anorg. Chem.*, **158,** 114 (1927).

(6) S. M. Jörgensen, *ibid.*, **2,** 281 (1892).

(7) S. P. L. Sørensen, *Biochem. Z.*, **21,** 186 (1909).

(8) H. W. Cowles, Jr., THIS JOURNAL, **30,** 1192 (1908).

(9) J. D. M. Smith, *Chem. Ind.*, **44,** 539T (1925).

of complex chlorine by aquation. A 1-g. sample was dissolved rapidly in 175 ml. of 0.33 *M* nitric acid, containing 100 g. of clear cracked ice in a 500-ml. glass stoppered Erlenmeyer flask; and then 25 ml. of 0.5 *M* silver nitrate was run in from a pipet, with shaking. The flask was stoppered and shaken vigorously for two minutes; the solution was then filtered rapidly with suction through two sheets of Whatman No. 42 filter paper supported on the sintered Jena glass disk of a suction funnel, care being taken to avoid transferring ice, which might contain unprecipitated chloride, to the funnel. Filtration was completed ten minutes after starting to dissolve the sample. After 6 to 10 washings with 0.001 *M* silver nitrate, the first silver chloride precipitate was discarded. The filtrate and washings, which appeared perfectly clear, were treated with 3 ml. of 30% hydrogen peroxide, heated to boiling, and boiled gently for fifteen minutes. This brought about complete decomposition of the complex ion. After standing overnight in a dark place, the second precipitate of silver chloride was collected and weighed.

Measurements with the Glass Electrode

For standardizing the glass electrode assembly, 0.05 *M* potassium biphthalate was used as our standard buffer. We have assumed that the *p*H of this solution at 25.0° is 3.983, as determined by MacInnes and Belcher.[10] To detect possible changes in the asymmetry potential of the glass membrane, standardizations were carried out at the beginning and end of each day's series of measurements (and in some cases more frequently).

The above-mentioned instability of the tetrammine ion made it necessary not only to determine the hydrogen ion concentration on a series of independent solutions, each with its quota of sodium hydroxide, but also to follow in each solution the change in potential of the glass electrode with time and to extrapolate these potentials back to the moment at which the solid ammine was added to the solution. It was assumed that the salt dissolved instantaneously, and that the relative amounts of diaquo and chloroaquo salts in the solution at that moment were the same as in the solid sample. In performing the extrapolation, it was necessary to take into account that in the large Pyrex container the ammine might decompose at a rate different from the rate in the glass electrode vessel, where the solution is exposed to a relatively large surface of soft, alkaline glass.

Details of a typical experiment are given in the following. Four buffer solutions (*i. e.*, mixtures of the diaquo chloride and sodium hydroxide) were generally prepared and measured on the same day. Approximately 1-liter samples of distilled water, contained in 2-liter Pyrex Erlenmeyer flasks, were boiled to remove carbon dioxide, cooled to room temperature under the protection of soda-lime tubes, weighed, and brought to 25.0° by standing overnight in the air thermostat. Measured volumes of standard 0.1 *M* sodium hydroxide were added from a recalibrated buret. Samples of diaquotetrammine chloride, which had been prepared on the same day, were weighed on watch glasses small enough to enter the necks of the 2-liter flasks. At the same time, samples were weighed for the determination of the percentage of cobalt.

At a suitable moment a stop-watch was started and the sample of ammine was dropped into the dilute alkali solution. This was immediately shaken very vigorously for sixty to ninety seconds. The glass electrode vessel was then rinsed three times and filled with the buffer solution; the time when the solution entered the glass spiral was noted. The first measurement of e. m. f. was in most cases made at four minutes by the stop-watch, but with the least stable buffers this time was reduced to two and one-half minutes. Measurements of e. m. f. were repeated at one and one-half to two and one-half minute intervals. At about ten minutes, and again at about twenty minutes, the buffer solution in the glass spiral was replaced by a fresh sample.

The observed values of e. m. f. were then graphically extrapolated in two steps: first, the values observed with each sample of the buffer were extrapolated to find the e. m. f. at the moment when this sample was run into the glass electrode; then these corrected values were extrapolated to zero time.

The slope of the extrapolation curve at zero time, $(dE/dt)_0$, may be taken as a measure of the instability of the buffer solution. In Fig. 1, values of $(dE/dt)_0$ (as read from the extrapolation curves) are plotted as a function of *p*H. It will be seen that the more acid solutions changed

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[10] Duncan A. MacInnes and Donald Belcher, THIS JOURNAL, **53**, 3326 (1931). This value conforms to the widely used, arbitrary *p*H scale defined by the specifications of W. Mansfield Clark, "The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins Co., Baltimore, 1928, p. 480. Dr. MacInnes has kindly pointed out (private communication, also *Cold Spring Harbor Symposia on Quantitative Biology*, **1**, 190 (1933)) that in accordance with his present point of view an agreement between *p*H measurement and thermodynamic ionization constants, etc., is best attained by shifting the scale by about 0.03 unit; the *p*H of the phthalate buffer is then 4.015. Adoption of this *p*H scale would result in raising the *p*H values reported in this paper by 0.032. When the individual dissociation constants in Table I are recalculated on this basis, the average values become $k_1 = 4.42 \times 10^{-6}$, $k_2 = 4.7 \times 10^{-8}$.

very slowly; with these, the change may have been due to a shift in the relative proportions of diaquo and chloroaquo ions. In solutions of higher *p*H, the more rapid changes were caused principally by decomposition of the complex ion; in such solutions a precipitate of cobalt hydroxide was formed on standing. The most alkaline buffer of this series, *p*H = 6.066, became perceptibly cloudy within thirteen minutes. This appeared to be the most alkaline buffer with which useful measurements could be made.

The *p*H values of the freshly prepared buffer solutions were finally calculated from the extrapolated values of e. m. f. In these calculations, the diffusion potential at the junction between buffer solution and saturated potassium chloride was neglected. The data which we have obtained are collected in Table I.

The first column of this table gives the volume of exactly tenth molar sodium hydroxide used in preparing a volume of buffer solution containing 0.004 mole of pure diaquo chloride; the second column gives the volume of this buffer solution; the third column gives the *p*H of the freshly prepared buffer solutions. (In correcting for the presence of chloroaquo chloride and other impurities, it is assumed that all samples of diaquo chloride crystals had the composition stated on page 385.)

TABLE I

BUFFER SOLUTIONS CONTAINING 0.004 MOLE OF $[Co(NH_3)_4(H_2O)_2]Cl_3$

Volume 0.1 *M* NaOH, ml.	Volume buffer soln., ml.	*p*H	*A*	$10^6 k_1$	$10^8 k_2$
36.17	1067	6.066	2.095	4.78	5.4
20.64	1050	5.335	2.483		
33.49	1069	5.925	2.162	4.79	4.6
12.84	1050	4.995	2.676		
30.41	1046	5.756	2.239	4.71	6.2
15.14	1019	5.105	2.620		
28.51	1066	5.684	2.287	4.71	4.3
7.64	1038	4.712	2.804		
28.09	1048	5.656	2.297	4.78	4.7
7.53	1021	4.697	2.807		
25.78	1059	5.553	2.355	5.00	(1.)
10.22	1042	4.844	2.741		
23.01	1038	5.436	2.424	4.8	(4.)
2.03	1026	4.183	2.932		
17.94	1052	5.223	2.550	4.82	(4.)
5.12	1039	4.513	2.864		
0.00	1034	3.915	2.969	(3.9)	...
.00	1011	3.866	2.966	(4.8)	...
.00	948	3.865	2.968	(4.5)	...
Average of accepted values				4.80	5.0

By plotting the *p*H values of these buffers as a function of the volume of tenth molar sodium hydroxide solution we obtain the titration curve shown in Fig. 2. This curve represents the titration of 0.004 mole of diaquotetrammine chloride in an average volume of solution of 1020 ml. (plus or minus about 2%).

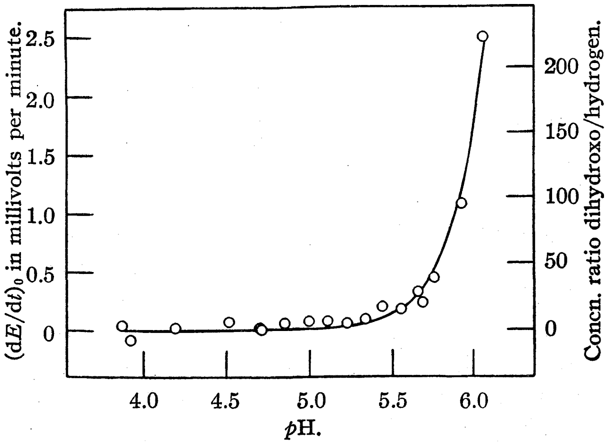

Fig. 1.

Calculation of Dissociation Constants

The primary and secondary dissociation constants of the cation acid, $Co(NH_3)_4(H_2O)_2^{+++}$, have been calculated from the data for titration with sodium hydroxide given in Table I. The method of calculation is similar to that outlined by Britton.[11] In these calculations, we have assumed the relation

$$pH = -\log h$$

(where *h* represents the concentration of hydrogen ions) as a sufficiently good approximation for our present purposes. As a result, the constants which we obtain are neither thermodynamic dissociation constants in terms of activities, nor classical dissociation constants in terms of true concentrations; they are approximately the same as the "acidity constants" defined by Brønsted.[12]

In the following discussion, brackets are used to denote concentrations; other symbols are tabulated below.

[+++]	concentration of $Co(NH_3)_4(H_2O)_2^{+++}$
[++]	concentration of $Co(NH_3)_4(H_2O)OH^{++}$
[+]	concentration of $Co(NH_3)_4(OH)_2^{+}$
b	concentration of added sodium hydroxide
c	total concentration of diaquotetrammine chloride
h	concentration of hydrogen ion

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[11] H. T. S. Britton, "Hydrogen Ions," Chapman and Hall, Ltd., London, 1929, page 150.

[12] J. N. Brønsted and Cecil V. King, *Z. physik. Chem.*, **130**, 700 (1927).

The primary and secondary dissociation constants, k_1 and k_2, are defined by the equations

$$k_1 = [^{++}]h/[^{+++}] \qquad (1)$$

$$k_2 = [^{+}]h/[^{++}] \qquad (2)$$

Since the total concentration of diaquotetrammine chloride is known, we may write

$$[^{+++}] + [^{++}] + [^{+}] = c \qquad (3)$$

From the law of electroneutrality we obtain the relation

$$3[^{+++}] + 2[^{++}] + [^{+}] + [H^+] + [Na^+] = [Cl^-] + [OH^-]$$

In the buffers included in these measurements, the concentration of hydroxyl ion is very small and may be neglected. The concentrations of Cl^- and Na^+ are known from the concentrations of the ammine and of the added hydroxide; the concentration of H^+ from the measurements of pH

$$[H^+] = h \quad [Na^+] = b \quad [Cl^-] = 3c$$

Substitution of these values in the above equation gives

$$3[^{+++}] + 2[^{++}] + [^{+}] = 3c - b - h \qquad (4)$$

By eliminating the unknown concentrations $[^{+++}]$, $[^{++}]$ and $[^{+}]$ from equations 1, 2, 3 and 4 we obtain the expression

$$\frac{3h^2 + 2k_1h + k_1k_2}{h^2 + k_1h + k_1k_2} = \frac{3c - b - h}{c} = A \qquad (5)$$

which defines the convenient function, A. Values of A, calculated from known values of b, c and h for the various buffer solutions, are listed in Table I.

By substituting in equation 5 values of h and A for two different buffer solutions in which these values are h_1, A_1 and h_2, A_2, we obtain a pair of simultaneous equations, from which, by elimination of k_2 or k_1, we obtain finally

$$k_1 = \frac{(A_1 - 1)(3 - A_2)h_2^2 - (A_2 - 1)(3 - A_1)h_1^2}{(A_1 - 1)(A_2 - 2)h_2 - (A_2 - 1)(A_1 - 2)h_1} \qquad (6)$$

and

$$k_2 = \frac{(A_2 - 2)(3 - A_1)h_1^2h_2 - (A_1 - 2)(3 - A_2)h_1h_2^2}{(A_1 - 1)(3 - A_2)h_2^2 - (A_2 - 1)(3 - A_1)h_1^2} \qquad (7)$$

The dissociation constants k_1 and k_2 may now be calculated by substituting numerical values in equations 6 and 7. The results of such calculations are presented in the last two columns of Table I. In selecting the different pairs of buffers to be used in these calculations, we have combined, wherever possible, measurements made on the same day using the same sample of ammine.

Correction for Chloroaquotetrammine Chloride

In the preceding calculations, chloroaquotetrammine chloride has been treated as an inert impurity. The chloroaquotetrammine ion, however, is presumably an acid of about the same strength as the hydroxoaquotetrammine ion, that is, an acid with a dissociation constant of the same magnitude as k_2. It is accordingly worth while to investigate how large an error in the values of k_1 and k_2 might have been caused by the presence of 1.65% of chloroaquo chloride in the samples of diaquo chloride.

Calling c' the total concentration of chloroaquotetrammine chloride and k' the dissociation constant of the chloroaquotetrammine ion as an acid, and inserting them in equations 3–5 above, we obtain as a corrected value of A

$$A' = \frac{3c - b - h}{c} + \frac{k'c'}{(k' + h)c} \qquad (8)$$

In the buffers of Table I the value of c' is 7×10^{-5}. If it is assumed that k' has the same value as k_2, we find that the maximum value of the correction to be applied to A (*i. e.*, in the case of the most alkaline buffer) amounts to 0.001. It is evident that in the present measurements this correction may be neglected.

Calculation of the Theoretical Titration Curve

To test the agreement between the individual measurements and the average calculated values of k_1 and k_2, we have computed the volumes of 0.1 M alkali which must be added to 0.004 mole of diaquo chloride in 1020 ml. of solution in order to produce buffer solutions having predetermined pH values. These are shown as small shaded circles in Fig. 2 and through them we have drawn the theoretical titration curve shown as a solid line. It can be seen that the observed values, shown as open circles, lie within 0.015 of a pH unit from this curve except in the case of those for solutions in pure water where in one instance the discrepancy is three times this amount.

To test this concordance still further we have constructed similar curves based on $k_1 = 4.3 \times 10^{-6}$ and 5.3×10^{-6} and $k_2 = 10^{-7}$ and 10^{-8} instead of our calculated values of 4.80×10^{-6} and 5×10^{-8}, respectively. These curves are shown as broken lines in the inserts in Fig. 2. Their distance from the curve through the observed points is several times the experimental error and justifies an estimate of the precision of our calculated values of k_1 and k_2 as about 2 and 20%, respectively.

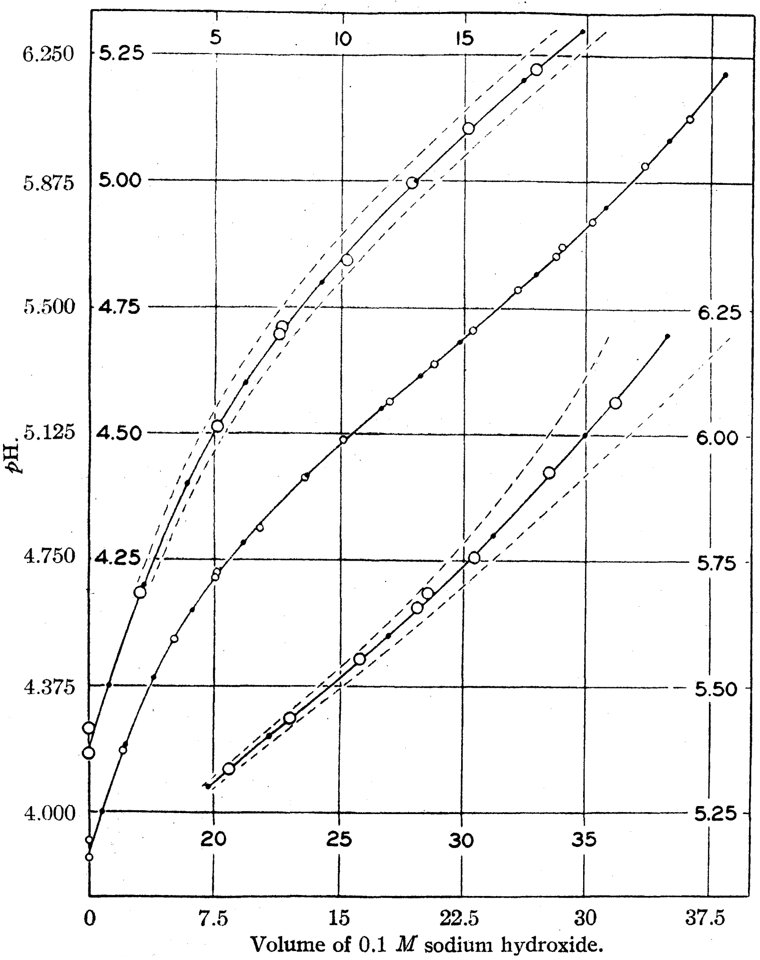

Fig. 2.—Titration curve of diaquotetrammine cobaltic ion: open circles, observed points; small shaded circles, points calculated for $k_1 = 4.8 \times 10^{-6}$, $k_2 = 5 \times 10^{-8}$. Inserts show same curve on 50% larger scale, with broken lines showing (upper insert) effect of varying k_1 between 4.3 and 5.3 $\times 10^{-6}$ and (lower insert) effect of varying k_2 between 10^{-7} and 10^{-8}.

Velocity of Decomposition

In conclusion, it should be pointed out that the data on the change in the potential of the glass electrode with time (used above in extrapolating to zero time) permit some interesting inferences regarding the decomposition of this ammine. The observed values of $(\mathrm{d}E/\mathrm{d}t)_0$ are a measure of the fraction of the hydrogen ions present in the solution which are neutralized in unit time;

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -\frac{RT}{F}\frac{\mathrm{d}\ln h}{\mathrm{d}t} = -\frac{RT}{F}\frac{1}{h}\frac{\mathrm{d}h}{\mathrm{d}t} \qquad (9)$$

Except for small changes resulting from shifts in the relative proportions of aquo and acido ions, this decrease in acidity undoubtedly reflects the liberation of ammonia from the ammine. From a comparison of Figs. 1 and 2, it is evident that the rate of this reaction, starting from approximately zero, begins to increase very rapidly at the pH value where k_2 first becomes important in determining the shape of the titration curve. This suggests that it is the dihydroxo ion which undergoes decomposition, and hence that the rate at which hydrogen ions are used up is proportional to the concentration of the dihydroxo ion;

$$-\mathrm{d}h/\mathrm{d}t = K[^+] \qquad (10)$$

Combination of equations 9 and 10 leads to

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{RT}{F}K\frac{[^+]}{h} \qquad (11)$$

This relation is tested by the solid curve shown in Fig. 1, which represents the variation with pH of the concentration ratio $[^+]/h$, as calculated for the average concentration of diaquotetrammine chloride in our solutions, using our values of k_1 and k_2. It can be seen that this curve runs very exactly through the observed values of $(\mathrm{d}E/\mathrm{d}t)_0$.

As a more explicit test of equation 10, we have computed from $(\mathrm{d}E/\mathrm{d}t)_0$ the actual change in hydrogen ion concentration in the nine least acid solutions, namely, in those solutions where the arithmetical change is not swamped by the experi-

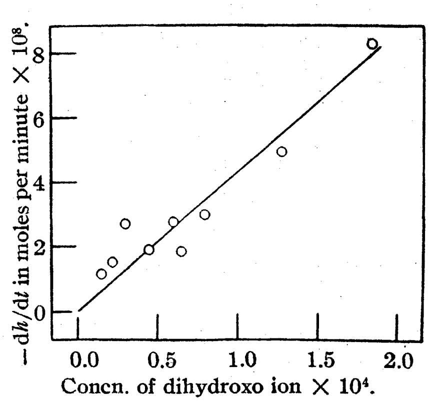

Fig. 3.

mental error. The resulting values are shown in Fig. 3, the straight line there drawn through the points being the best one as determined by the method of least squares. Its equation is

$$-dh/dt = 4.3 \times 10^{-4}\,[+] \qquad (12)$$

The concordance of these points with a straight line indicates that the reaction of decomposition is unimolecular with respect to the dihydroxotetrammine ion.

Summary

It has been shown:

1. That concordant values of the dissociation constants of diaquotetrammine cobaltic ion as an acid can be obtained by measuring with the glass electrode the concentration of hydrogen ion in solutions of this ammine ion to which various amounts of sodium hydroxide have been added.
2. That the velocity of decomposition of this ion in these solutions is proportional to the first power of the concentration of the dihydroxotetrammine ion in equilibrium with it, as computed from these values of the dissociation constants.

CAMBRIDGE, MASS. RECEIVED DECEMBER 12, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

The Lead–Uranium–Thorium Ratio of a Single Crystal of Wilberforce Uraninite

BY CHESTER M. ALTER AND LAURA A. YUILL

It has been shown recently[1] that the composition of a single crystal of uraninite from near Wilberforce, Cardiff Township, Ontario, may not be uniform throughout the crystal. Ellsworth[2] has found the same phenomenon in the case of Villeneuve uraninite. It is interesting to note that in both cases the percentage of thorium is highest in the outer portion of the crystal, decreases toward the interior and then increases again in the core. The variation in thorium content was not great in the case of the Villeneuve crystal but was very noticeable in the Wilberforce crystal. The lead and thorium contents showed certain irregularities which were also difficult to explain, especially by any process of leaching.

Alter and Kipp removed succeeding layers of the crystal by dissolving in nitric acid. In spite of the fact that this dissolution was done very rapidly, it was thought possible that there may have been preferential leaching throughout the crystal while any one layer was being dissolved. In that case the results would be meaningless, as definite layers of the crystal would not have been removed for analysis. In order to preclude such a possibility it was decided to repeat the work by analyzing various layers which had been mechanically removed from a single crystal rather than by acid dissolution.

For this purpose a rather well-developed crystal, a part of a large collection of material from the Wilberforce locality,[3] weighing approximately 42 g., was obtained from Professor Alfred C. Lane. According to Dr. H. V. Ellsworth[4] this material was collected from Pit 4[5] where the uraninite occurs in a gangue of fluorite and calcite. He further reports that the uraninite from this pit is considerably altered. This specimen, however, apparently carried very little of the usual surface alteration products and exhibited very distinct crystal faces and angles. A spot of apparently foreign material appeared on one face, and this proved to penetrate well into the core of the crystal.

The crystal was divided into three parts—outer, middle, and core—by carefully removing successive parts by means of a steel file. Each face was filed down an equal amount, great effort being taken to maintain the original form of the crystal during the process of filing off the outer portions. The outside, middle, and core portions weighed, respectively, 12.7 g., 15.2 g., and 13.5 g.

The particles of steel introduced in the samples were removed by very thorough magnetic separation.

The analytical procedures for the determination of lead, thorium, and uranium were in general those described in detail by Alter and Kipp.[1] Approximately one-gram samples were dissolved

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[1] Alter and Kipp, *Am. J. Sci.*, **32**, 120 (1936).

[2] Ellsworth, *Am. Mineral.*, **15**, 455 (1930).

[3] Report of Committee on Measurement of Geologic Time by Atomic Disintegration, National Research Council, Division of Geology and Geography, May 3, 1930.

[4] Private communication.

[5] Ellsworth, Canadian Geological Survey, Econ. Geol. Series, No. 11, pp. 214, 221 (1932).

in nitric acid, evaporated to dryness, diluted, the insoluble material filtered off, ignited, and weighed. The lead was precipitated from acid solution as sulfide, converted to sulfate, and weighed. Uranium and thorium were twice precipitated as hydroxide. After the combined hydroxides were dissolved in nitric acid, the thorium was precipitated as oxalate, dissolved in nitric acid, and precipitated as thorium sebacate with sebacic acid. The thorium sebacate was dissolved and reprecipitated, washed free from sebacic acid, ignited, and weighed as ThO_2. Iron and aluminum were removed from the uranium solution by precipitation with ammonium carbonate. The uranium was precipitated as ammonium uranate, ignited, and weighed as U_3O_8.

Unusual precaution was taken to carry out precipitations under best conditions to ensure purity. Filtrates were all evaporated and tested for desired constituents.

TABLE OF RESULTS

Section of crystal	Analysis	Insoluble, %	Lead,[6] %	Uranium, %	Thorium, %	$\frac{Pb}{U+0.36Th}$
Outside	1	2.01	9.16	52.98	5.24	
	2	1.99	9.14	53.11	5.22	
	3	2.00		52.88	5.21	
	Av.	2.00	9.15	52.99	5.22	0.1668
Av. Alter and Kipp			9.74	37.85	8.36	.2383
Middle	1	0.93	10.17	54.41	15.26	
	2	.95	9.96	54.46	15.24	
	3	.94	10.06	54.53	15.25	
	Av.	.94	10.06	54.47	15.25	.1678
Av. Alter and Kipp			11.93	58.48	14.09	.1877
Core	1	1.24	10.98	55.51	10.40	
	2	1.28	11.05	55.48	10.45	
	3	1.27	11.11		10.52	
	Av.	1.26	11.05	55.50	10.46	.1864
Av. Alter and Kipp			11.87	60.70	8.05	.1866
Weighted av. for whole crystal			10.10	54.36	10.61	.1736
Av. Alter and Kipp			11.13	47.73	9.55	.2175

Discussion

The ratio Pb/(U + 0.36Th) of the outer layer indicates that the crystal had not been subjected to surface alteration since it is commonly found that any leaching process tends to cause a rise in this ratio. The higher ratio in the core of the crystal is unusual.

The variation of the thorium content in various sections of the crystal is of great interest. It will be seen that this variation is of the same magnitude and direction as that noticed by Alter and Kipp.[1] Since this phenomenon exists in all three cases where methods have been used that would detect it, it would be of great interest to examine, in a like manner, crystals of uraninite from other localities.

The ratios obtained by Alter and Kipp and those reported here are slightly higher than those reported for Wilberforce material by Todd[7] and Ellsworth.[8,2] The latter[9] has pointed out that this is no doubt due to the fact that the Lane material from Pit No. 4 and analyzed in this Laboratory is of inferior quality compared with that analyzed earlier by Todd and by Ellsworth and which was obtained from Pit No. 1.[5] However, it has been observed that the two uraninite-bearing bodies of Pits 1 and 4 are not visibly connected although they are in line.

The results emphasize the necessity for careful selection of material in order to obtain reliable data for age calculations. Erroneous results may be obtained if even a single crystal in its entirety is ground and analyzed. Based on the age formula:

$$\text{Age} = \frac{\log(U + 0.36Th + 1.155Pb) - \log(U + 0.36Th)}{6.6 \times 10^{-5}} \text{ million years}$$

the discrepancy in age using the data for the whole crystal and those for the core amounts to approximately eighty million years, while the discrepancy between the ages calculated for the whole crystal and outside portion is about forty million years. These errors, although large, lose some of their impressiveness when they are compared with the age of this mineral, which is calculated by the above formula to be between 1100 and 1200 million years.

A part of this work was supported by a grant from the National Research Council, for which the authors wish to acknowledge gratitude.

Summary

1. Determinations of the lead–uranium–thorium ratio of sections of a single crystal of uraninite removed mechanically confirm earlier results in which the sections were removed by acid solution.

2. The composition of a single crystal of uraninite may vary exceedingly, especially in regard to thorium content.

3. The results may throw some light on the conditions in the pegmatite during crystallization.

BOSTON, MASS. RECEIVED JANUARY 14, 1937

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(6) 206.195 was used for the atomic weight of lead. See Baxter and Bliss, THIS JOURNAL, **52**, 4851 (1930).

(7) See Bull. 80, p. 328, The National Research Council, 1931.

(8) Ellsworth, *Am. J. Sci.*, (5) **9**, 127 (1925).

(9) Private communication.

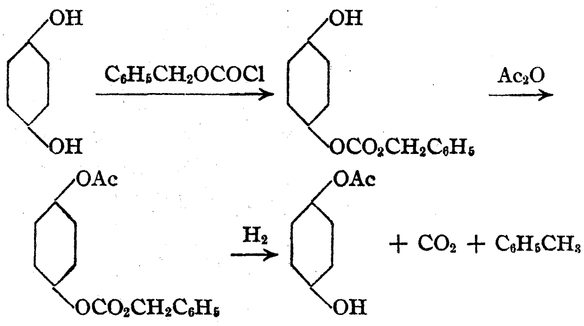
[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA]

Monoacetates of Hydroquinone and Catechol

BY H. S. OLCOTT

In the course of studies on antioxidants in fats[1] we wished to investigate, among other phenolic compounds, hydroquinone and catechol monoacetates, and could find no references to their preparation or properties. Preliminary attempts at synthesis with limited quantities of an acetylating reagent yielded appreciable amounts of the diacetates. The successful use of benzyl chloroformate by Bergmann and Zervas[2] in the synthesis of peptides suggested that this reagent might also be useful in the preparation of the compounds mentioned above. Carbobenzoxy esters, prepared by means of benzyl chloroformate, can be split by hydrogen in the presence of a platinum or palladium catalyst, thus avoiding the hydrolyzing action of acids or bases.

The monoacetate of hydroquinone or catechol was prepared easily by a series of reactions involving the preparation of the monocarbobenzoxy derivative, acetylation of the remaining hydroxyl, and removal of the carbobenzoxy group by hydrogenation.



It was later found possible, and much more practicable, to obtain the monoacetates in fair yields by careful acetylation of the dihydroxy compounds in aqueous solution. However, the methods used in the first syntheses are described inasmuch as they may prove useful in more complicated synthetic procedures.

Experimental

The benzyl chloroformate[3] was prepared as directed by Bergmann and Zervas.

Monocarbobenzoxyhydroquinone.—A mixture of 2 g. of hydroquinone and 1 g. of sodium carbonate was dissolved in 30 cc. of water in a 200 cc. rubber-stoppered bottle kept filled with nitrogen. To this solution was added 3.5 g. of benzyl chloroformate in several portions. Between the additions the bottle was shaken in a mechanical shaker. When the reaction was complete, as indicated by the disappearance of the odor of benzyl chloroformate, the solid product was filtered, washed with water, dissolved in alcohol, boneblacked and crystallized from 50% alcohol. The white, irregular flat prisms melted at 120–120.5°[4]; yield, approximately 50%.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.8; H, 5.0. Found: C, 68.8; H, 5.5.

Dicarbobenzoxyhydroquinone.—This compound was prepared by a similar procedure except that double the quantities of sodium carbonate and benzyl chloroformate were used. The insoluble reaction product crystallized from hot alcohol in the form of fine white needles, m. p. 142–143°.

Anal. Calcd. for $C_{22}H_{18}O_6$: C, 69.8; H, 4.8. Found: C, 69.6; H, 5.2.

Dicarbobenzoxyhydroquinone in alcohol was hydrogenated in the presence of a platinum catalyst.[5] The catalyst was removed and the alcohol evaporated to dryness. The residue was identified as hydroquinone, by the m. p. of the impure product, 163°, and of the sublimed crystals, 169°.

Monocarbobenzoxyhydroquinone Monobenzoate.—Monocarbobenzoxyhydroquinone was dissolved in five parts of pyridine to which was added one part of benzoyl chloride. The mixture was allowed to stand overnight and then poured into an excess of water. The precipitate was filtered, washed and recrystallized from alcohol. The fine white platelets melted at 97–98°.

On hydrogenation, monocarbobenzoxyhydroquinone benzoate yielded hydroquinone monobenzoate which, after crystallization from 70% alcohol, melted at 160°. A mixture with a specimen synthesized by the method of Robertson and Waters[6] melted at 160–161°.

Monocarbobenzoxyhydroquinone Monoacetate.—Monocarbobenzoxyhydroquinone (1 part) was quantitatively acetylated with acetic anhydride (1 part) in pyridine (5 parts) by standing at room temperature for twelve hours. The precipitate which formed when the mixture was poured into water was filtered, washed and recrystallized from small amounts of alcohol in which it tended to form supersaturated solutions. The minute colorless crystals melted at 75–76°.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.1; H, 5.0. Found: C, 67.2; H, 5.2.

Hydroquinone Monoacetate. Method 1.—Monocarbobenzoxyhydroquinone monoacetate was hydrogenated in

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(1) Olcott, THIS JOURNAL, **56**, 2492 (1934).

(2) Bergmann and Zervas, *Ber.*, **65**, 1192 (1932).

(3) Dr. R. M. Conrad kindly supplied this reagent.

(4) All melting points are corrected.

(5) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 452.

(6) Robertson and Waters, *J. Chem. Soc.*, 2729 (1930).

alcohol with a platinum catalyst. Palladium[5] and Raney nickel[7] were also effective but hydrogen was absorbed more slowly. When absorption had ceased, the catalyst was filtered and washed with alcohol, and the filtrate was evaporated to dryness. The residue was crystallized from large amounts of petroleum ether (b. p. 60–70°).

Method 2.—Hydroquinone was acetylated with the equivalent of one mole of acetic anhydride following the directions of Chattaway[8] for the preparation of acetates except that sodium carbonate was substituted for sodium hydroxide. Stirring was continued for an hour after the addition of the last of the acetic anhydride and the mixture was then allowed to stand at room temperature overnight. The hydroquinone diacetate, amounting approximately to 30% of the original hydroquinone, was filtered off. The filtrate was extracted with ether, and the ether layer was washed, dried with anhydrous sodium sulfate and evaporated to dryness. The residue was extracted repeatedly with boiling petroleum ether, from which, on cooling, hydroquinone monoacetate crystallized in colorless irregular prisms, m. p. 62–63°.

Hydroquinone monoacetate is very soluble in water, alcohol and ether. The aqueous solution gives no color with ferric chloride.

Anal. Calcd. for $C_8H_8O_3$: C, 63.1; H, 5.3. Found: C, 63.1; H, 5.6.

On further acetylation, hydroquinone monoacetate yields the diacetate, m. p. 120.5–121°; mixed m. p. with a product obtained from hydroquinone and an excess of acetic anhydride, 121°.

Monocarbobenzoxycatechol.—This compound, prepared by procedures similar to those used for the analogous hydroquinone derivative, crystallized from petroleum ether (b. p. 60–70°) in rosets of colorless needles, m. p. 88.5–89°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.8; H, 5.0. Found: C, 69.1; H, 5.1.

Monocarbobenzoxycatechol Monoacetate.—On pouring the mixture used to acetylate monocarbobenzoxycatechol into water, a colorless oil separated. This was extracted with ether. The ether layer was washed, dried and evaporated to dryness and the residue distilled in high vacuum (0.1 mm.). Only 2 cc. was distilled and a satisfactory distilling temperature was not recorded; most of the material distilled between 100–150°.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.1; H, 5.0. Found: C, 67.2; H, 5.0.

Catechol Monoacetate.—Prepared by both methods outlined under hydroquinone monoacetate, catechol monoacetate was obtained as a colorless oil which did not crystallize at low temperatures. Traces of catechol were removed by crystallization from petroleum ether in which the monoacetate is more soluble. The monoacetate distilled approximately at 130–140° (0.1 mm.).

Anal. Calcd. for $C_8H_8O_3$: C, 63.1; H, 5.3. Found: C, 62.9; H, 5.5.

Catechol monoacetate possesses a slight phenolic odor and is soluble in water, alcohol, ether and petroleum ether. Dilute aqueous solutions give a green color with ferric chloride. On acetylation, the diacetate of m. p. 60° is obtained.

Antioxidant Properties.—All of the compounds described were assayed for their antioxygenic properties by determining the effect of adding small amounts to lard. The method used for measuring the length of the induction period has been described previously.[1,9] Only the monoacetates showed any protective effect (Table I). The monoacetate of catechol was more effective than that of hydroquinone, in contrast to the results with the monomethyl esters of these two phenols.[1,10] Other monoesters of hydroquinone are ineffective.[1] Neither monoacetate approaches the effectiveness of the original dihydroxy compounds. In view of the fact that catechol monoacetate could not be purified by crystallization, its antioxygenic effect might have been due to traces of catechol.

TABLE I

ANTIOXIDANT PROPERTIES OF THE MONOACETATES OF HYDROQUINONE AND CATECHOL IN LARD

Amount of added substance, %		Induction period (75°), hrs. With inhibitor	Without inhibitor
0.02	Hydroquinone monoacetate	19	18
.02		25	22
.02		15	11
.10		52	11
.02	Catechol monoacetate	52	18
.02		62	22
.01	Hydroquinone[9]	410	14
.01	Catechol[11]	408	9

The author is indebted to Lever Brothers Company for a grant in support of this research.

Summary

Hydroquinone and catechol monoacetates have been prepared by careful acetylation of the diphenols and also with the use of carbobenzoxy derivatives. Catechol monoacetate is more effective as an antioxidant than hydroquinone monoacetate but much less effective than either catechol or hydroquinone.

IOWA CITY, IOWA RECEIVED DECEMBER 21, 1936

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[7] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[8] Chattaway, *J. Chem. Soc.*, 2495 (1931).

[9] French, Olcott and Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935).

[10] Mattill, *J. Biol. Chem.*, **90**, 141 (1931).

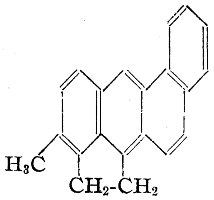
[11] These results are representative. Duplicate runs would be subject to the variations previously described [Olcott and Mattill, THIS JOURNAL, **58**, 1627 (1936)].

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Aceanthrene Derivatives Related to Cholanthrene

BY LOUIS F. FIESER AND E. B. HERSHBERG[1]

It was reported in a paper by one of us with Seligman[2] that the methyl group of methylcholanthrene (I) is not important in determining the high carcinogenic potency of this hydrocarbon, for cholanthrene (II) produces transplantable tumors only slightly less rapidly than methylcholanthrene.[2,3] Fieser and Newman[4] investigated further simplifications of the molecule, and it was found that 5,10-dimethyl-1,2-benzanthracene (III) retains the properties characteristic of methylcholanthrene and produces tumors regularly and with great rapidity. Dr. M. J. Shear has confirmed the preliminary report[4] and found that the hydrocarbon has about the same activity as methylcholanthrene, producing in mice transplantable tumors which appear, on the average, after about three months. The five-membered ring present in the cholanthrenes evidently is not important in determining the biological action of the compounds, and it is not even essential for high activity that both methyl groups be retained. Dr. Shear has found that 10-methyl-1,2-benzanthracene[4] (IV) is comparable in carcinogenic activity with the hydrocarbons I–III. Injected subcutaneously into mice in 5-mg. dosage, the hydrocarbon gave tumors which made their first appearance in two months. At the end of four months, tumors had been obtained in fifteen of twenty mice. Three of these tumors were transplanted successfully. In contrast to this powerful agent, 5-methyl-1,2-benzanthracene produces tumors only slowly[5] and is more nearly comparable with 1,2,5,6-dibenzanthracene than with the cholanthrenes.



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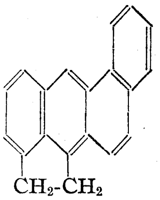

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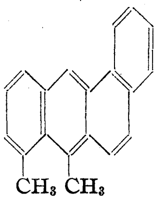
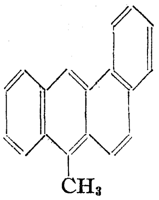


III



IV

From these results it is evident that the carcinogenic potency of methylcholanthrene cannot be attributed to a special pentacyclic structure, as was suggested by the early work of Cook and his associates,[3b] or to the fact that the hydrocarbon is a 1,2-benzanthracene derivative with alkyl substituents at the 5- and 6-positions. From the present results it appears that the structural feature of greatest importance is the presence of a simple carbon substituent at the meso position 10 in the 1,2-benzanthracene ring system. In comparison with the effect of such a group, the influence of alkyl substituents at the 5- and 6-positions[5] is of secondary significance. Evidently the size and structure of the substituent at the 10 position is of considerable importance, for the English investigators[5] found that 10-isopropyl- and 10-benzyl-1,2-benzanthracene are devoid of carcinogenic activity. The contrasting effects of methyl and isopropyl groups at position 10 are surprising in view of the observation[5] that 6-methyl-1,2-benzanthracene is somewhat inferior in carcinogenic properties to the 6-isopropyl compound. The 5-*n*-propyl compound, however, was found to give fewer tumors than the 5-methyl derivative.[3a] The relationship between the 10-methyl and 10-isopropyl compounds appears to be comparable also with that between the highly potent methylcholanthrene and the slowly acting 16,20-dimethylcholanthrene.[6] The latter hydrocarbon, which carries a larger and more branched substituent at the meso position, produces tumors which appear in about the same average time[7] as in the case of 1,2,5,6-dibenzanthracene (seven and one-half months). It is clearly important to explore further the relationship of structure and carcinogenic activity in the series of 10-alkyl-1,2-

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(1) Lilly Research Fellow.

(2) Fieser and Seligman, THIS JOURNAL, **57**, 2174 (1935).

(3) (a) Cook, *Ber.*, **69A**, 38 (1936); (b) Cook, Haslewood, Hewett, Hieger, Kennaway and Mayneord, Reports of the II International Congress of Scientific and Social Campaign against Cancer, **1**, 1 (1936).

(4) Fieser and Newman, THIS JOURNAL, **58**, 2376 (1936).

(5) Barry, Cook, Haslewood, Hewett, Hieger and Mayneord, *Proc. Roy. Soc.* (London), **B117**, 318 (1935).

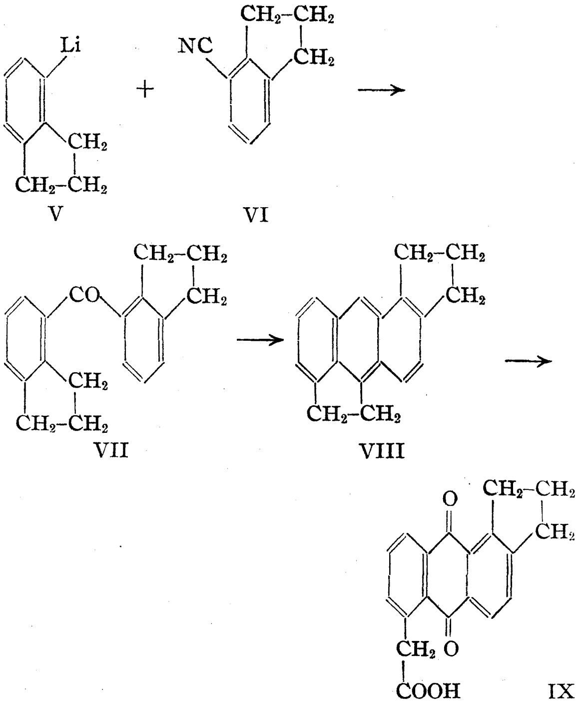
(6) Fieser and Seligman, THIS JOURNAL, **57**, 1377 (1935).

(7) Shear, *Am. J. Cancer*, **28**, 334 (1936).

benzanthracenes, and such work is in progress.[8] It is interesting that the powerfully carcinogenic 3,4-benzpyrene may be regarded as a 1,2-benzanthracene with a carbon substituent at the alternate meso position 9, and that 8,9-dimethylene-1,2-benzanthracene[2] shows some activity, producing tumors in an average time of about seven months.[7] The influence of a methyl group at the 9-position is being investigated in independent work by Dr. M. S. Newman.

It is hoped that by defining the features of structure associated with high carcinogenic activity, some clue may be found which will help to reveal the nature of the action of cancer-producing hydrocarbons on cellular tissue. The recognition that the potency of methylcholanthrene is retained in compounds of much less complicated structure may serve at least to clarify the problem. In order to provide as sound a basis for speculation as possible, it seemed desirable to determine whether 10-methyl-1,2-benzanthracene represents a limiting structure beyond which the process of simplification cannot be carried without great loss in activity. The 10-methyl group clearly is important, for the parent hydrocarbon is almost completely inactive.[5] It is conceivable that the angular aromatic ring attached to the anthracene system in the 1,2-position may be subject to modification, for the 5,6-dimethyl- and 5,6-cyclopenteno derivatives of 1,2-benzanthracene are comparable with 1,2,5,6-dibenzanthracene in carcinogenic activity.[5] In order to test this point we have synthesized for comparison with cholanthrene one hydrocarbon differing from this substance in having two methyl groups in place of the angular benzenoid ring, and another one having a cyclopenteno ring in the 1,2-position.

For the synthesis of 1,2-cyclopenteno-5,10-aceanthrene (VIII), 4-chlorohydrindene was prepared from *o*-chlorobenzaldehyde through the known 4-chlorohydrindone-1[9] and a part of the material was converted into the lithium derivative V, while a part was transformed into 4-cyanohydrindene (VI) by interaction with cuprous cyanide in pyridine solution. By the condensation of V and VI and hydrolysis of the resulting ketimine, the ketone VII was obtained in a crystalline condition. Since the ketone is symmetrical, the Elbs reaction theoretically can proceed in only one direction, and the sole product found in the reaction mixture was the hydrocarbon VIII. The yield of nearly pure material was 21%, which is considerably better than is usually obtained in the Elbs condensation of *o*-methylated diphenyl ketones. On the other hand, the pyrolysis proceeds less smoothly than in the methylcholanthrene synthesis,[10] where the cyclopenteno ring involved in the cyclization interacts with a naphthoyl, rather than a benzoyl, group. The structure of the hydrocarbon was established by oxidation in glacial acetic acid solution to the anthraquinone acetic acid derivative IX.



1,2-Dimethyl-5,10-aceanthrene (XII) was obtained along with the isomeric 1-methyl-5,6-cyclopentenoanthracene (XIII) by the pyrolysis of the ketone (XI) resulting from the condensation of 4-cyanohydrindene with the Grignard reagent (X) from *vic.*-bromo-*o*-xylene. The hydrocarbons were isolated in a satisfactory condition of purity only in very small amounts and oxidation experiments were completed only in the case of the lower melting isomer. This yielded a neutral anthraquinone having the full complement of carbon atoms, and therefore it must have come from 1-methyl-5,6-cyclopentenoanthracene (XIII). The other hydrocarbon probably has the alternate

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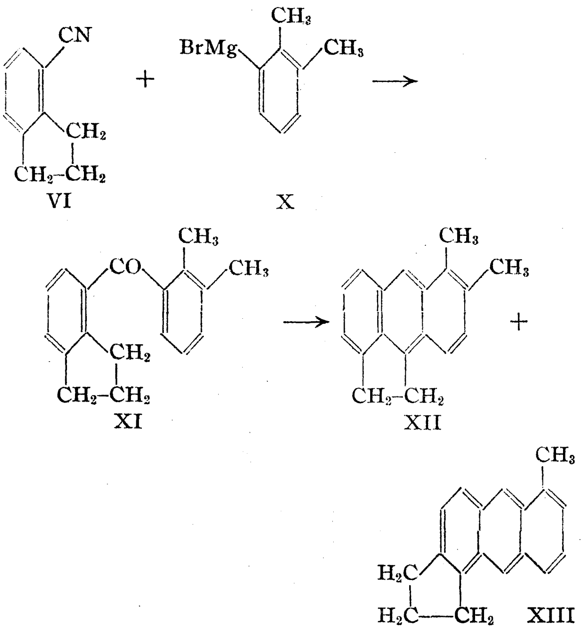
[8] 10-Methyl-1,2-benzanthracene has been prepared from 1,2-benz-10-anthrone and methylmagnesium iodide, a method previously investigated without success by Cook, *J. Chem. Soc.*, 1089 (1930). The 10-ethyl compound, m. p. 113.5–114°, corr., has been prepared in a similar manner.

[9] Mayer, Philipps, Ruppert and Schmitt, *Ber.*, **61**, 1966 (1928).

[10] Fieser and Seligman, (a) THIS JOURNAL, **57**, 942 (1935); (b) **58**, 2482 (1936).



structure XII, but this was not established rigidly. An acidic substance giving a strong vat test was formed on oxidation, but it was not obtained in a pure condition.

In tests conducted by Dr. M. J. Shear 1,2-cyclopenteno-5,10-aceanthrene (VIII), injected subcutaneously into mice, has given no tumors in four months. Tests with the hydrocarbons XII and XIII have been negative after two months. No tumors have been obtained with aceanthrene[11] in one and one-half years.

Experimental Part[12]

4-Chlorohydrindene.—*o*-Chlorocinnamic acid was prepared from *o*-chlorobenzaldehyde, acetic anhydride, and potassium acetate according to the procedure of Lasch.[13] In experiments in which the heating was conducted for eight hours and for fourteen hours, the yields of recrystallized material, m. p. 207–209°, were 62 and 56%, respectively. The product was accompanied by a resinous substance insoluble in sodium carbonate solution. *o*-Chlorohydrocinnamic acid[14] was prepared by the catalytic hydrogenation of 77 g. of the unsaturated acid in 500 cc. of warm dioxane, using a total of 1 g. of Adams catalyst. The reaction proceeded to completion in about ten hours, the course of the reduction being followed most satisfactorily by precipitating the material with water from a test portion of the solution and determining the melting point. A small amount of unchanged acid raises the melting point and is detected easily. Continued hydrogenation beyond the desired point leads to an inferior product. The yield of satisfactory material, m. p. 93–95°, was 95%. A sample recrystallized from benzene–ligroin melted at 94.5–95.5°. For conversion to β-(*o*-chlorophenyl)-propionyl chloride[9] 70 g. of the acid was refluxed for three hours with 136 g. of purified thionyl chloride, the excess reagent was distilled, and the product was obtained as a colorless liquid, b. p. 147.5–149° (26 mm.); yield 73 g. (95%). A solution of this material (73 g.) in 1800 cc. of carbon bisulfide was cooled to 5° and 66 g. of aluminum chloride was added with vigorous mechanical stirring. The resulting light yellow solution was allowed to come to room temperature in one and one-half hours, during which time a white complex separated. After refluxing for fifteen minutes the product was collected in the usual way and taken into ether–benzene. The solution was washed in succession with dilute acid, dilute alkali, and saturated sodium chloride solution, and after removal of the solvent the product was distilled. The yield of colorless 4-chlorohydrindone-1,[9] b. p. 123–124° (5 mm.), m. p. 89–90.5° (recrystallized, 90–90.5°), was 55.5 g. (93%).

The Clemmensen reduction of the ketone (114 g.) was conducted exactly as described for the preparation of 4-methyl-7-chlorohydrindene.[10] The yield of 4-chlorohydrindene, b. p. 108–110° (24 mm.), was 93 g. (89%). Material for use in the formation of the lithium derivative was further purified by shaking it repeatedly with successive, equal, portions of concentrated sulfuric acid until an impurity which at first imparted to the acid a brilliant scarlet coloration was largely removed. Little material was lost in the process.

4-Cyanohydrindene.—Following the procedure described in an analogous case,[10b] 46 g. of the 4-chlorohydrindene heated with 27.8 g. of cuprous cyanide and 40 cc. of pyridine at 220° for seventeen hours, gave 34.5 g. (80%) of redistilled nitrile, b. p. 139–141° (22 mm.). The higher boiling material remaining after distillation of the nitrile boiled at about 120–180° (22 mm.) and proved to be largely the corresponding **amide.** Crystallized from alcohol, it formed long, flat, colorless needles, m. p. 173–173.5°, and it was identical with a sample prepared by the reaction of the acid chloride with aqueous ammonia solution.

Anal. Calcd. for $C_{10}H_{10}NO$: C, 74.49; H, 6.89. Found: C, 74.09; H, 6.60.

The nitrile proved very resistant to acid hydrolysis, refluxing with 6 *N* hydrochloric acid for two days giving only a small amount of the acid. When 1 g. of the nitrile was heated with 15 cc. of concentrated hydrochloric acid for ten hours at 180–200° there was some carbonization and 0.8 g. of **hydrindene-4-carboxylic acid** was obtained. Recrystallized from dilute alcohol, the acid formed flat needles, m. p. 152.5–153.5°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.03; H, 6.24. Found: C, 73.69; H, 6.16.

Di-(4-hydrindyl) Ketone (VII).—For the manipulation of lithium metal it was found convenient to prepare wire of uniform diameter in a sodium press equipped with a 3-mm. die. The wire is collected under heavy paraffin oil and cut into uniform 12-cm. lengths, which are placed in a test-tube having a stopcock at the bottom and a nitrogen inlet near the stopper. The sticks of metal are washed with successive portions of benzene and ether under nitrogen pressure, draining the wash liquor through the stop-

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[11] Fieser and Peters, THIS JOURNAL, **54**, 4373 (1932).

[12] All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

[13] Lasch, *Monatsh.*, **34**, 1653 (1913).

[14] Gabriel and Herzberg, *Ber.*, **16**, 2037 (1883).

cock. The wire is calibrated by weighing one of the sections, or a part thereof. The lithium is introduced to the reaction flask after this has been flushed with nitrogen and with the gas streaming from the widest opening of the flask. While flushing the opened lithium container with nitrogen, the test-tube is held at right angles to the mouth of the flask, a length of lithium wire is withdrawn and short cylinders are cut with scissors and allowed to drop into the flask. Fresh, silvery surfaces are thus exposed and protected until the other reactants are added.

The reaction between 4-chlorohydrindene (12.1 g.) and lithium (1.1 g.) in ether (75 cc.) started at once without the use of catalysts but proceeded slowly owing to the formation of an adherent coating on the metal. After stirring the mixture under nitrogen for eighteen hours, titration of a 1-cc. portion indicated 71% conversion to the aryl lithium. There was little change at the end of forty hours (75% conversion), and the solution was cooled to −70° and 10 g. of 4-cyanohydrindene in 25 cc. of ether was added rapidly. The solution was allowed to come to room temperature and refluxed for one hour to complete the reaction. The mixture was decomposed with dilute hydrochloric acid, using in all about 100 cc. of 3 *N* acid, the ether was evaporated, 5 cc. of glacial acetic acid was added to facilitate the hydrolysis of the ketimine hydrochloride, and the mixture was refluxed for four hours. The ketone was taken into ether and the solution was filtered from a little suspended material and distilled, affording 10.5 g. (51%) of ketone, b. p. 206–209° (4 mm.). The distillate solidified completely and on crystallization from petroleum ether the compound formed large, colorless prisms, m. p. 77–78°.

Anal. Calcd. for $C_{19}H_{18}O$: C, 87.33; H, 6.93. Found: C, 86.88; H, 7.00.

1,2-Cyclopenteno-5,10-aceanthrene (VIII).—Two lots of the ketone VII, totaling 13.3 g., were pyrolyzed separately at 415–420° for thirty minutes and the product was distilled in vacuum and crystallized from ligroin. The crude, yellow hydrocarbon obtained melted at 160–170° and weighed 2.6 g. (21%). For purification a solution of the material in benzene–ligroin was passed through an adsorption tower of activated alumina, which removed some foreign material. The process was repeated and the material from the first portion of the filtrate after two crystallizations from ligroin formed pale yellow needles melting at 175.5–176° (0.3 g.). The bulk of the material, similarly crystallized, melted at 174–176° (1.7 g.). The hydrocarbon forms a light yellow, fluorescent solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.70; H, 6.99.

The picrate crystallized from ligroin in the form of purplish black needles, m. p. 140.5–141.5°. The regenerated hydrocarbon was unchanged in melting point.

Anal. Calcd. for $C_{19}H_{16}\cdot C_6H_3O_7N_3$: N, 8.88. Found: N, 8.69.

1,2 - Cyclopenteno - 9,10 - anthraquinone - 5 - acetic Acid (IX).—A solution of 0.65 g. of 1,2-cyclopenteno-5,10-aceanthrene and 3.5 g. of sodium dichromate in 35 cc. of glacial acetic acid was refluxed for two hours and the solution was diluted with a large volume of water. The precipitated material (0.35 g.) formed pale yellow microplates on crystallization from xylene. When heated rapidly, the substance melts with decomposition at 284–285°. It is soluble in hot, dilute soda solution and gives a red vat with alkaline hydrosulfite.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.54; H, 4.61. Found: C, 74.75; H, 4.38.

On attempting to decarboxylate the acid with copper carbonate in quinoline solution there was much decomposition and only a small amount of an impure neutral quinone, m. p. 121–123°, was isolated.

***vic.*-Bromo-*o*-xylene.**—The preparation of this halide by sulfonating *o*-xylene,[15] brominating the resulting 4-sulfonic acid, and hydrolyzing the bromo sulfonic acid is reported by Stallard,[16] but experimental details are lacking. After some investigation, the following procedure was developed.

A mixture of 106 g. of *o*-xylene and 107 cc. of concentrated sulfuric acid was heated on the steam-bath with mechanical stirring for one and one-half hours and the clear solution was dissolved in one and one-half liters of water. The solution was rendered neutral to litmus with 473 g. of hydrated barium hydroxide dissolved in about 750 cc. of water and the solution was filtered hot, cooled to 50–60°, and treated with a solution of 192 g. of bromine and 200 g. of barium bromide in 700 cc. of water. The temperature of the solution was maintained at 50–60° for fifteen hours, during which time barium 2-bromo-1,2-dimethylbenzene-4-sulfonate separated. The solid was collected after cooling, washed well with water, and air dried; yield, 225 g. This amount of pure salt (trihydrate) would correspond to a yield of 63%, but from the results of hydrolysis it is evident that the product contained some *o*-xylene sulfonate.

The hydrolysis with superheated steam was conducted in a distillation apparatus constructed with interchangeable ground-glass joints. The joint between the copper coil superheater and the glass inlet tube was made satisfactorily with a brass compression fitting, using alternate layers of asbestos and lead wool as packing. A total of 693 g. of barium salt was hydrolyzed in three lots, each of which was mixed with about 300 cc. of sulfuric acid, sp. gr. 1.67, in the distillation flask. The inlet steam was at 200–220° and the exit vapor was held at 150–160°. With the use of an automatic separatory take-off, the aqueous portion of the distillate was discarded and the heavy layer of oil was collected. The oil was washed with water, dried and fractionated twice through a 1-meter packed column. About 40 g. of *o*-xylene was recovered and the yield of *vic.*-bromo-*o*-xylene, b. p. 210.5–212.5°, was 149 g. (42%, calculated on the basis of pure barium salt).

4 - (2′,3′ - Dimethylbenzoyl) - hydrindene (XI).—An ethereal solution of the Grignard reagent from 48 g. of *vic.*-bromo-*o*-xylene was added to an ice-cold solution of 26.1 g. of 4-cyanohydrindene in ether. Considerable heat was liberated and the precipitate first formed largely dissolved. After refluxing the mixture overnight in an atmosphere of nitrogen a clear red solution resulted. This was treated with 3 *N* hydrochloric acid, the ether was distilled, and the mixture was refluxed for four hours to effect hydrolysis. An ethereal extract of the ketone was

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(15) Jacobsen, *Ber.*, **10**, 1011 (1877); **11**, 17 (1878).

(16) Stallard, *J. Chem. Soc.*, **89**, 808 (1906). See also Kelbe and Stein, *Ber.*, **19**, 2137 (1886).

washed with water, dried with saturated sodium chloride solution, and distilled, giving 38.3 g. of a yellow oil, b. p. 183–186° (4 mm.). which slowly solidified. On crystallization from petroleum ether (b. p. 20–40°), 25.6 g. (56%) of the ketone was obtained in a satisfactory condition, m. p. 74–75°. A sample recrystallized from the same solvent formed large, colorless cubes melting at 75–75.5°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.49; H, 7.24. Found: C, 86.63; H, 7.32.

1,2 - Dimethyl - 5,10 - aceanthrene (XII) and 1-Methyl-5,6-cyclopentenoanthracene (XIII).—The ketone XI (20.5 g.) was pyrolyzed at 420–430° for two hours and the product was distilled in vacuum and taken up in petroleum ether (b. p. 20–40°). On standing at 0° a crystalline product (0.84 g.) consisting largely of the crude dimethylaceanthrene slowly separated. This was purified by passage of a solution in benzene through an adsorption tower of alumina, conversion to the picrate, regeneration with ammonia solution, and crystallization of the hydrocarbon from ligroin. **1,2-Dimethyl-5,10-aceanthrene** was obtained as pale yellow, glistening leaflets melting at 206–207°; yield 0.25 g. (1.3%).

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.35; H, 6.45.

The picrate formed long, permanganate-colored needles from benzene–ligroin and melted at 169–170°.

Anal. Calcd. for $C_{18}H_{16}\cdot C_6H_3O_7N_3$: N, 9.11. Found: N, 8.96.

On refluxing a solution of 50 mg. of the hydrocarbon and 200 mg. of sodium dichromate in 5 cc. of glacial acetic acid for one hour and adding water, there was obtained a brown precipitate which partly dissolved in carbonate solution. This solution gave a strong vat test on adding sodium hydrosulfite, but the amount of product was insufficient for more definite characterization.

The second hydrocarbon, **1-methyl-5,6-cyclopentenoanthracene,** was isolated as the picrate from the initial petroleum ether mother liquors, after first removing extraneous material by purification in an adsorption tower. After repeated crystallization from benzene–ligroin, the **picrate** formed deep brownish red needles, m. p. 156–157°.

Anal. Calcd. for $C_{18}H_{16}\cdot C_6H_3O_7N_3$: N, 9.11. Found: N, 8.80.

The regenerated hydrocarbon, after crystallization from ligroin, formed pale-yellow blades melting at 131–132°; yield, 0.58 g. (3%).

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.94; H, 6.87.

Oxidation to **1-methyl-5,6-cyclopentenoanthraquinone** was accomplished by refluxing a solution of 50 mg. of the hydrocarbon and 300 mg. of sodium dichromate in 5 cc. of glacial acetic acid for one hour and precipitating the product with water. The crude quinone was purified by crystallization from dilute alcohol, vacuum sublimation, and recrystallization from dilute alcohol. It formed long, slender, light yellow needles, m. p. 125–127°. Like other di-α-substituted anthraquinones, the compound does not give a vat test with hydrosulfite in aqueous alkali.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.49; H, 5.38. Found: C, 82.20, 82.18; H, 5.35, 5.56.

Summary

Tests with the previously described 5,10-dimethyl-1,2-benzanthracene and 10-methyl-1,2-benzanthracene indicate that these hydrocarbons are of the same order of carcinogenic potency as methylcholanthrene and cholanthrene, from which it appears that methylcholanthrene owes its high activity to the presence of the 1,2-benzanthracene ring system with a simple alkyl substituent at the 10-position. In order to determine if further simplifications of the structure can be made without loss in potency, 1,2-cyclopenteno-5,10-aceanthrene and 1,2-dimethyl-5,10-aceanthrene have been synthesized for comparison with cholanthrene (1,2-benz-5,10-aceanthrene), and biological tests are in progress.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

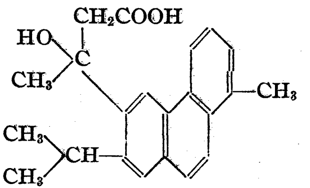
Investigations in the Retene Field. VIII. The Synthesis of 3′-Methyl-5,6-cyclopentenoretene

BY DAVID E. ADELSON[1] AND MARSTON TAYLOR BOGERT

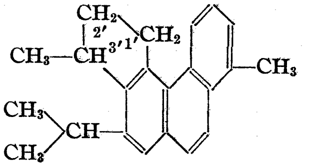
In a preliminary communication[2] announcement was made of the synthesis of 3′-methyl-5,6-cyclopentenoretene using 6-acetylretene[3] as the starting material. At that time attention was called to the fact that such a polycyclic hydrocarbon should be of interest because it arose as a synthetic product of retene, itself a natural product containing methyl and isopropyl groups which apparently have a very significant function in nature. Furthermore, 3′-methyl-5,6-cyclopentenoretene was shown to be of interest because it is a methyl isopropyl homolog of Diels' hydrocarbon[4] which has been the subject of much scientific investigation because of its isolation as a dehydrogenation product of a wide variety of naturally occurring materials.

It is of significance that retene was used for comparative purposes in preliminary work on the structure of Diels' hydrocarbon. Rosenheim and King[5] pointed out the striking similarity between the ultraviolet absorption spectra of Diels' hydrocarbon and retene and cited this fact as conclusive proof that this $C_{18}H_{16}$ was a phenanthrene derivative. Bernal and Crowfoot[6] suggested that Diels' hydrocarbon was a methylcyclopentenophenanthrene because of the striking similarity of the cell dimensions of this $C_{18}H_{16}$ to those of retene.

The Reformatsky reaction between 6-acetylretene, ethyl bromoacetate and zinc dust yielded a hydroxy ester which was hydrolyzed to β-hydroxy-β-6-retylbutanoic acid (I). The latter was further characterized by the preparation of its methyl ester. The hydroxy acid (I) was dehydrated by means of acetic anhydride to β-6-retylcrotonic acid which was then reduced to β-6-retylbutanoic acid. Cyclization of the acid chloride of the latter through the agency of aluminum chloride in benzene solution gave 1′-keto-3′-methyl-5,6-cyclopentenoretene which was characterized by the preparation of its oxime. This cyclic ketone was converted into 3′-methyl-5,6-cyclopentenoretene (II) by means of the Clemmensen reduction.



(I)



(II)

Inasmuch as 6-acetylretene was used as the starting material, the structure of 3′-methyl-5,6-cyclopentenoretene was defined at once. C_7 being occupied by the isopropyl group, only C_5 was available for ring closure. Solutions of 3′-methyl-5,6-cyclopentenoretene exhibited no fluorescence. Hillemann[7] has reported similar findings for three isomeric methylcyclopentenophenanthrenes.

The picrate of 3′-methyl-5,6-cyclopentenoretene was found to be unstable, being readily split into its components on repeated recrystallization. This is similar to the behavior of the picrate of 3′-methyl-1,2-cyclopentenophenanthrene.[8,9,10]

The physiological properties of 3′-methyl-5,6-cyclopentenoretene are being studied and will be reported at an early date.

Acknowledgment.—Our thanks are due to the Hooker Electrochemical Company, Niagara Falls, N. Y., for a generous supply of anhydrous aluminum chloride.

Experimental

β-Hydroxy-β-6-retylbutanoic Acid.—To a solution of 10 g. of 6-acetylretene and 17 g. of ethyl bromoacetate in 40 cc. of dry benzene, there was added 14 g. of zinc dust and a few crystals of iodine and the resulting mixture was carefully heated to the boiling point. After the initial vigorous reaction had subsided somewhat, the mixture was refluxed for three hours, cooled and poured onto a mixture of

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[1] National Research Fellow in Chemistry.

[2] Adelson and Bogert, *Proc. Natl. Acad. Sci.*, **23**, in press (1937).

[3] Adelson and Bogert, THIS JOURNAL, **57**, 653 (1936).

[4] Diels, Gädke and Körding, *Ann.*, **459**, 1 (1927).

[5] Rosenheim and King, *Chemistry and Industry*, **52**, 299 (1933).

[6] Bernal and Crowfoot, *ibid.*, **52**, 729 (1933); *J. Chem. Soc.*, 93 (1935).

[7] Hillemann, *Ber.*, **69**, 2610 (1936).

[8] Harper, Kon and Ruzicka, *J. Chem. Soc.*, 124 (1934).

[9] Gamble, Kon and Saunders, *ibid.*, 644 (1935).

[10] Ruzicka and Thomann, *Helv. Chim. Acta*, **16**, 226 (1933).

cracked ice and 10% sulfuric acid. The benzene layer was separated, washed successively with 10% sulfuric acid, water, 5% sodium carbonate solution and water and the solvent was removed. The brown oil which remained could not be induced to crystallize. It was dissolved in 80 cc. of methanol containing 10 g. of potassium hydroxide and the resulting solution was refluxed for four hours. Most of the methanol was removed in a current of air, water added and the solution acidified. A brown precipitate (11.4 g.) formed. Recrystallized from a mixture of chloroform and petroleum ether (b. p. 40–60°), β-hydroxy-β-6-retylbutanoic acid appeared as fine, white crystals which melted with decomposition at 118–119° (corr.); yield, 8 g. Further recrystallization raised the melting point to 121–122° (corr.) where it remained constant.

Anal. Calcd. for $C_{22}H_{24}O_3$: C, 78.52; H, 7.20. Found: C, 78.24; H, 7.44.

Methyl Ester.—This was prepared and worked up as described above from 3.5 g. of 6-acetylretene, 6 g. of methyl bromoacetate and 5 g. of zinc dust in 30 cc. of dry benzene. After removal of the benzene, there remained an oil which solidified upon standing to a pale yellow solid; yield, 4 g. From 95% ethanol methyl β-hydroxy-β-6-retylbutanoate appeared as tiny, pale yellow crystals, m. p. 90–90.5° (corr.).

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.81; H, 7.48. Found: C, 78.59; H, 7.32.

β-6-Retylcrotonic Acid.—A mixture of 10 g. of β-hydroxy-β-6-retylbutanoic acid, 20 g. of anhydrous sodium acetate and 75 cc. of freshly distilled acetic anhydride was refluxed for three hours, cooled and poured into 500 cc. of water. After the acetic anhydride had been destroyed and the aqueous solution removed by decantation, the crude solid was boiled with 400 cc. of 1% potassium hydroxide solution and filtered. Acidification precipitated 9 g. of a pale brown solid. Recrystallized from an ethanol–water mixture (norite), β-6-retylcrotonic acid appeared as short, white needles, m. p. 205–206° (corr.) with decomposition; yield, 7 g. An acetone solution of the unsaturated acid decolorized a solution of potassium permanganate in acetone.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.98; H, 6.97. Found: C, 83.25; H, 7.15.

β-6-Retylbutanoic Acid.—Eight grams of β-6-retylcrotonic acid was dissolved in 110 cc. of absolute methanol containing 2 g. of potassium hydroxide and 180 g. of 3% sodium amalgam was added. The resulting mixture was refluxed for six hours, allowed to stand overnight and filtered. Dilution of the filtrate followed by acidification yielded 8 g. of solid material. β-6-Retylbutanoic acid crystallized from a petroleum solvent[11] as small, glistening white plates, m. p. 152.5–153.5° (corr.); yield, 7 g.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.45; H, 7.56. Found: C, 82.60; H, 7.50.

1′-Keto-3′-methyl-5,6-cyclopentenoretene.—A mixture of 10 g. of β-6-retylbutanoic acid, 7 g. of powdered phosphorus pentachloride and 75 cc. of dry benzene was stirred and refluxed for one hour, cooled and 6.7 g. of anhydrous, powdered aluminum chloride was added in portions with stirring. The resulting mixture was stirred one-half hour at room temperature, then two and one-half hours at gentle reflux, cooled and poured onto cracked ice containing some concentrated hydrochloric acid. The benzene was removed by steam distillation and the viscous solid that remained behind was extracted with 350 cc. of 3% potassium carbonate solution. Acidification of the carbonate filtrate yielded 2 g. of unchanged β-6-retylbutanoic acid. The carbonate-insoluble residue was dissolved in 75 cc. of *n*-propanol, a hot solution of 7 g. of picric acid in 40 cc. of *n*-propanol was added and the mixture boiled for five minutes. The picrate that separated on cooling was recrystallized twice from 95% ethanol and the keto compound was regenerated by distribution between a 5% sodium carbonate solution and ether; yield, 3 g. Recrystallized from a petroleum solvent[11] and then from 95% ethanol, 1′-keto-3′-methyl-5,6-cyclopentenoretene appeared as short, pale yellow needles, m. p. 111.5–112.5° (corr.).

Anal. Calcd. for $C_{22}H_{22}O$: C, 87.37; H, 7.34. Found: C, 87.08; H, 7.57.

Oxime.—A suspension of 0.4 g. of the above ketene, 0.8 g. of hydroxylamine hydrochloride and 1.2 g. of anhydrous barium carbonate in 25 cc. of absolute methanol was refluxed for eight hours, filtered and the filtrate diluted with water. This precipitated the oxime in nearly theoretical yield. Recrystallized from dilute ethanol, it appeared as short, white needles which darkened somewhat at 192° (corr.) and melted with decomposition at 194–195° (corr.).

Anal. Calcd. for $C_{22}H_{23}ON$: C, 83.23; H, 7.31. Found: C, 82.96; H, 7.32.

3′-Methyl-5,6-cyclopentenoretene.—A mixture of 1.6 g. of 1′-keto-3′-methyl-5,6-cyclopentenoretene, 9 g. of amalgamated zinc and 20 cc. of concentrated hydrochloric acid was refluxed for twenty-four hours, an additional 5 cc. of acid being added after twelve hours. The pale yellow oil that resulted was taken up in ether, the ethereal solution washed with 10% hydrochloric acid, water and the solvent evaporated. The residue was dissolved in hot 95% ethanol, a hot solution of 1.9 g. of picric acid in 95% ethanol was added and the resulting picrate was twice recrystallized from absolute ethanol. The hydrocarbon (1 g.) was recovered by distribution of the picrate between a 5% sodium carbonate solution and ether. Recrystallized from an ethanol–water mixture, 3′-methyl-5,6-cyclopentenoretene appeared as short, white needles, m. p. 74.5–75.5° (corr.). The hydrocarbon was soluble in the common organic solvents and in vegetable oils.

Anal. Calcd. for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.52, 91.95; H, 8.68, 8.73.

Picrate.—This was prepared by mixing hot solutions of 0.174 g. of the pure hydrocarbon and 0.146 g. of picric acid each in 4 cc. of absolute ethanol and boiling for five minutes. The picrate crystallized out in quantitative yield on cooling. Recrystallized from absolute ethanol, it appeared as bright orange needles, m. p. 154–155° (corr.). The picrate of 3′-methyl-5,6-cyclopentenoretene was readily split into its components on repeated recrystallization.

Anal. Calcd. for $C_{28}H_{27}O_7N_3$: C, 64.96; H, 5.26. Found: C, 64.36; H, 5.43.

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[11] B. p. 77–115°. The solvent gave no coloration when shaken with concentrated sulfuric acid.

Summary

1. Hydrolysis of the product obtained in the Reformatsky reaction between 6-acetylretene and ethyl bromoacetate yields β-hydroxy-β-6-retylbutanoic acid.

2. Dehydration of this acid followed by reduction gives β-6-retylbutanoic acid whose acid chloride yields upon cyclization 1′-keto-3′-methyl-5,6-cyclopentenoretene.

3. The Clemmensen reduction of this cyclic ketone yields 3′-methyl-5,6-cyclopentenoretene.

NEW YORK, N. Y. RECEIVED JANUARY 9, 1937

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

A Series of Aliphatic Dimethyl Amides[1]

BY JOHN R. RUHOFF[2] AND E. EMMET REID

Dimethyl amides have been prepared by several investigators,[3] but the data on them are incomplete and not correlated. It seemed desirable to make a complete series of them so that comparisons can be made, not only between individual compounds, but also between this and other series. The eight dimethyl amides of the normal acids from formic to caprylic have been prepared and characterized. An unexpected discovery was that the acids except formic and their dimethyl amides give azeotropes boiling 4–5° *above* the amides. The data are in Table I and II. All of these dimethyl amides are mobile liquids which mix in all proportions with carbon disulfide, chloroform, carbon tetrachloride, benzene, ether, acetone and alcohol. The first two have limited solubility in petroleum ether, while the others mix with it. The lower members mix with water, but the higher homologs become increasingly insoluble; the solubility of VIII in water is less than 1%. In these respects dimethyl amides resemble esters, except that they are much more soluble in water and boil at substantially higher temperatures than esters of the same carbon content.

Another object was to investigate further the method of preparation of dimethyl amides recently proposed by Mitchell and Reid.[4] Repetition of their work showed that dimethyl amides are formed in liberal amounts by their procedure, but that the reactions are not complete, except with formic acid. Fractionation, taking very close cuts, gave what appeared to be pure compounds, but these proved to be azeotropic mixtures of the dimethyl amides and the acids. These azeotropes caused Mitchell and Reid to overestimate their yields and troubled van der Zande.[5] The data on these constant boiling mixtures are brought together in Table II.

Experimental

Two equivalents of gaseous dimethylamine was passed into an acid which was heated under a reflux condenser from the top of which the excess of amine passed to a water trap. The water in the condenser jacket was kept warm enough to permit water vapor to escape. When there seemed to be no further reaction, the product was fractionated through a six-foot (2 meter) precision still,[6] a narrow cut being taken at what appeared to be the boiling point. The products were found to contain free acid which was titrated with the results given in Table II. Several experiments were made with acetic acid, noting the temperature of the boiling mixture, and titrating samples of it after successive portions of amine had been added. No matter how much amine was passed in the liquid in the flask never became neutral.

Dimethyl acetamide was obtained in 78% yield by heating 360 g. of acetic acid, saturated with gaseous dimethylamine at 35°, for five hours at 200° in a steel bomb. Solid caustic potash was added to the product to take up water and acetic acid. The liquid thus purified was distilled at 162–165°; it was then dried and fractionated taking the cut 164.8–164.9° at 759 mm. Analysis showed this to be 99.25% pure. The dimethyl amides of butyric, heptoic and caprylic acids were made similarly. With the higher acids a new difficulty was encountered; the potassium salt of the acid is soluble in the dimethyl amide. In such cases the reaction product was taken up in a large volume of benzene and this solution shaken with potassium hydroxide solution, dried and distilled. Franchimont and Klobbie prepared heptoic dimethyl amide by this method.

Other dimethyl amides were obtained in good yields by adding the acid chloride dropwise during three hours to a

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(1) From a part of the Ph.D. dissertation of John R. Ruhoff, 1932.

(2) Kewaunee Manufacturing Company Fellow in Chemistry, 1929–33.

(3) (a) A. P. N. Franchimont, *Rec. trav. chim.*, **2**, 332 (1883); (b) A. P. N. Franchimont and E. A. Klobbie, *ibid.*, **6**, 247 (1887); (c) A. P. N. Franchimont and H. A. Rouffaer, *ibid.*, **13**, 336 (1894); (d) A. Verley, *Bull. soc. chim.*, [3] **9**, 690 (1893); (f) *J. Russ. Phys.-Chem. Soc.*, **29**, 227 (1897); (e) M. Tiffeneau and K. Fuhrer, *Bull. soc. chim.*, [4] **15**, 169–170 (1914).

(4) Mitchell and Reid, THIS JOURNAL, **53**, 1879 (1931).

(5) Van der Zande, *Rec. trav. chim.*, **8**, 233 (1889).

(6) Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

TABLE I

PHYSICAL PROPERTIES OF THE DIMETHYL AMIDES

Amide	M. p.,[a] °C.	B. p., °C.	Press., mm.	d^0_4	d^{25}_4	n^{25}_D	M_D, obsd.	At. ref.[b] of N
I[c]	−61	153.0	760	0.9683	0.9445	1.4269	19.84	2.60
II[d]	−20	165.0	758	.9599	.9366	1.4351	24.24	2.49
III	−45	175.5	765	.9429	.9203	1.4371	28.75	2.40
IV[e]	−40	124.5	100	.9279	.9064	1.4391	33.39	2.43
V	−51	141.0	100	.9178	.8962	1.4419	38.08	2.52
VI	−42	158.0	100	.9099	.8896	1.4430	42.62	2.46
VII[f]	−19	172.5	100	.9051	.8854	1.4450	47.19	2.43
VIII	−21	187.0	100	.9002	.8810	1.4471	51.87	2.50
							Average	2.49

[a] The freezing points were determined with a copper–constantan thermocouple and potentiometer. [b] Obtained by subtracting the sum of the atomic refractions of all the atoms except nitrogen (Getman and Daniels, "Outlines of Theoretical Chemistry," p. 93) from the observed M_D. [c] Verley (ref. 3d) gives b. p. 155° and d^{20} 0.968; Franchimont and Rouffaer (ref. 3c) give b. p. 153° and sp. gr. 0.9525 at 15°; Bruhl [*Ph. Ch.*, **22,** 375 (1897)] gives b. p. 76° at 39 mm., $d^{22.4}_4$ 0.9484, and $n^{22.4}_D$ 1.42938. By interpolation our densities are 0.9493^{20}_4, 0.9540^{15}_4, and $0.9469^{22.4}_4$. [d] Franchimont (ref. 3a) gives b. p. 165.5° at 754 mm. and d^{20} 0.9405; Bruhl (*Ph. Ch.*, **22,** 376 (1897)) gives b. p. 83–84° at 32 mm., d^{20}_4 0.9434, and $n^{22.5}_D$ 1.43708. Our (calcd.) value is d^{20}_4 0.9413. [e] Tiffeneau and Fuhrer (ref. 3e) give b. p. 186–196°. Franchimont and Klobbie (ref. 3b) give b. p. 242.5–243.5° at 758 mm., and sp. gr. 0.894^{15}, our d^{15}_4 0.893.

TABLE II

AZEOTROPIC MIXTURES OF ACIDS AND THEIR DIMETHYL AMIDES

Amide	Boiling range, °C.	Pressure, mm.	Amide, %	Acid, %	Sum
I	153.2	757	97.4	1.2	98.6
II	170.8–170.9	761	77.2	21.1	98.3
III	179.2–179.4	767	75.8	23.4	99.2
IV	129.9–130.0	100	66.1	32.0	98.1
V	145.7–145.9	100	68.0	30.8	98.8
VIII	189.9–190.0	100	71.9	26.0	97.9

TABLE III

ANALYTICAL DATA

Amide	Carbon, %		Hydrogen, %	
	Calcd.	Found	Calcd.	Found
III	59.35	59.40	10.97	11.35
V	65.05	65.67	11.71	11.65
VI	67.07	67.61	11.97	11.76
VIII	70.10	69.73	12.37	12.26

concentrated aqueous solution of three moles of the amine kept at −20 to −10°. The resulting mixture was saturated with potassium hydroxide in the cold, and the dimethyl amide separated and distilled.

The analyses of the new dimethyl amides, propionic, *n*-valeric, caproic and caprylic are given in Table III.

Acknowledgment.—The authors wish to express their thanks to the du Pont Company for the dimethylamine solution, to Mr. W. D. Thompson for the semi-micro analyses, and to Messrs. Ferry, Hall and D'Alelio for assistance.

Summary

The first eight members of the series of normal aliphatic dimethyl amides have been prepared and their more common physical properties measured.

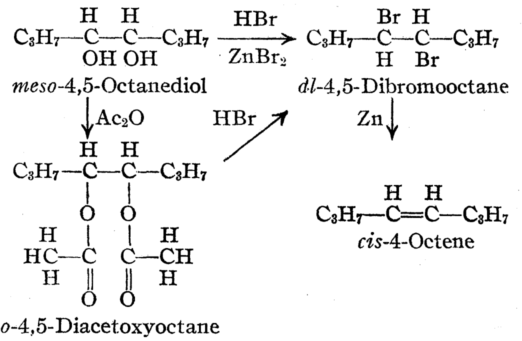
BALTIMORE, MARYLAND RECEIVED NOVEMBER 14, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Investigations on the Stereoisomerism of Unsaturated Compounds. III. The Preparation of the *cis* and *trans* 4-Octenes[1]

BY WILLIAM G. YOUNG, ZENE JASAITIS AND LEO LEVANAS

The *cis* and *trans* 4-octenes were prepared from the *dl*- and *meso*-4,5-dibromooctanes by the method of Gladstone and Tribe as modified by Wilkinson.[2] The 4,5-dibromooctanes were obtained from the *meso*- and *dl*-4,5-octanediols in two ways: (a) by the direct action of a reagent made by saturating an aqueous solution of zinc bromide with hydrogen bromide at 20° and (b) by the action of hydrobromic acid (saturated at 0°) on the diacetates of the *dl*- and *meso*-4,5-octanediols. The reactions involved are as follows



$$\begin{tikzcd}
dl\text{-4,5-Octanediol} \arrow[r, "HBr", "ZnBr_2"'] \arrow[d, "Ac_2O"] & meso\text{-4,5-Dibromooctane} \arrow[d, "Zn"] \\
dl\text{-4,5-Diacetoxyoctane} \arrow[ru, "HBr"'] & trans\text{-4-Octene}
\end{tikzcd}$$

The dibromooctane derived from the meso glycol by the HBr–$ZnBr_2$ method was first throught to be a mixture of both *meso* and *dl* modifications since it boiled over a considerable range (83–98° at 4.5 mm.) and contained the correct quantity of bromine by Carius analysis. The fact that this bromide gave a mixture of octane and octene when treated with zinc and alcohol brought still more concern for it indicated that this reagent had caused a partial replacement of bromine by hydrogen. A reduction of this type had never been observed by the authors in dealing with similar dibromo compounds. However, when the dibromooctanes, prepared from the 4,5-diacetoxyoctanes, were treated with zinc in alcohol they produced only 4-octene. It was therefore considered unlikely that the octane mentioned above was formed by the reduction of the 4,5-dibromooctane in the previous sample. A discussion of these results with Professor H. J. Lucas of the California Institute of Technology brought out the fact that the HBr–$ZnBr_2$ treatment of the 2,3-butanediols gave very poor yields of dibromide. On the other hand, a ketone was formed as the result of a pinacolone rearrangement. In our case the rearrangement undoubtedly was followed by replacement of hydroxyl by bromine before ketone formation occurred, thus giving rise to 4,4-dibromooctane. In order to separate the mixture of 4,4- and 4,5-dibromooctanes the material was converted into a mixture of octene and octane which was then treated with bromine. The dibromide thus formed was separated from the octane by distillation. The product collected was identical with the *dl*-4,5-dibromooctane obtained from *meso*-4,5-octanediol by the diacetate method. The HBr–$ZnBr_2$ method proved to be the most satisfactory for the preparation of the dibromide from the *meso*-glycol and the HBr–diacetate method was best for the dibromide from the *dl*-glycol.[3]

The Configuration of Compounds Involved in the Synthesis of the *cis* and *trans*-4-Octenes.—Since previous work[4] on the reaction of stereoisomeric dibromides with potassium iodide in ethyl or methyl alcohols has shown that the meso isomer has the higher reaction rate, we have concluded from the specific second order reaction rate constants, k_2, for the 4,5-dibromooctanes,[5] that the value of $k_2 = 0.0996$ for the dibromide from the *meso*-4,5-octanediol shows that it is the *dl*-modification while the value of $k_2 = 0.1268$ for the dibromide from the *dl*-4,5-

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[1] This paper was presented before the Organic Division at the ninety-second meeting of the American Chemical Society held in Pittsburgh, Pa., September 7–11, 1936. The work was accomplished with the aid of a grant from the Board of Research of the University of California.

[2] Wilkinson, *J. Chem. Soc.*, 3057–62 (1931).

[3] This procedure was tried at the suggestion of Professor H. J. Lucas who had found that the 2,3-dibromobutanes could not be prepared by the HBr–$ZnBr_2$ method, Wilson and Lucas, THIS JOURNAL, **58**, 2396 (1936).

[4] (a) Van Duin, *Rec. trav. chim.*, **45**, 345–62 (1926); (b) Dillon, Young and Lucas, THIS JOURNAL, **52**, 1953–64 (1930).

[5] The details of this work, together with that on other dibromides, will be published elsewhere.

octanediol shows that it is the *meso* isomer. Obviously, a change in configuration has taken place in going from the glycols to the dibromides. A similar change in configuration has been observed in the case of the 2,3-butanediols by Lucas and Wilson.[3] It should be noted that only one of the asymmetric carbon atoms is involved in the inversion. If both asymmetric carbons were involved, the configuration change would not be apparent.

Fortunately, it is possible to confirm the conclusion that the *dl*-glycol gives the *meso*-dibromide. The *meso*-4,5-dibromooctane having the higher reaction rate should give the higher melting *trans*-4-octene and the *dl*-4,5-dibromooctane should give the lower melting *cis*-4-octene. The melting points of the octenes were found to be in agreement with the prediction.

Since the formation of the *meso*-4,5-dibromooctane from the *dl*-glycol involves two steps the question naturally arises: At which step does the change of configuration take place? A comparison of physical properties such as density and refractive index of the 4,5-diacetoxyoctanes with those of other known *meso*- and *dl*-stereoisomers leads to the conclusion that the *meso*-glycol gives the *meso*-diacetate. Work is now in progress in this Laboratory in which the dextrorotatory 4,5-octanediol is being converted into the diacetate and thence into the dibromooctane. The optical rotation is being followed at each step.

The Synthesis of Normal cis-trans-Alkenes

Although the preparation of alkene hydrocarbons has received much attention in the literature, it has been recognized only in recent years that the usual methods of preparation of olefins give rise to mixtures of structural as well as geometrical isomers.[6] In spite of the fact that this problem of dealing with mixtures has been partially solved by the development of (a) high precision fractionating columns and (b) synthetic methods which give rise to pure products, nevertheless, only the pure *cis*- and *trans*-butenes and pentenes are known.[7] Although several *cis*-isomers of the higher molecular weight normal alkenes have been prepared,[8] no pure *trans*-isomers have been obtained. Both the bromo-ether method[9] and the unsaturated acid method[7] of preparing alkenes give rise to pure structural isomers, but, unfortunately, fractionation of the intermediate or final products into their geometrical isomers becomes more difficult as the molecular weight increases in the homologous series. Schmitt and Boord[6a] have pointed out the fact that the apparent nonexistence of *cis–trans* isomerism in the case of 2-hexene and 3-hexene is due to the similarity in boiling point of the isomers. In the present paper it may be noted that the isomeric 4-octenes also have identical boiling points. The work of Lucas and Prater[7d] indicates that the unsaturated acid method has another disadvantage. The α-ethylcrotonic acids were prone to form equilibrium mixtures readily, a difficulty which was not encountered with the α-methylcrotonic acids.[7b] If this tendency to undergo stereomutation increased with molecular weight, it would be very difficult to isolate and keep the *cis* and *trans* acids necessary in the preparation of the isomeric normal hexenes and heptenes.

Although the action of zinc on dibromoalkanes has been used frequently in the purification of alkenes,[10] this procedure ordinarily has not been used in the preparation of pure *cis* and *trans* isomers since the usual source of the pure isomeric dibromides has been the hydrocarbons themselves. However, the method has been used in the synthesis of the polyene hydrocarbons[11] and now that it is feasible to obtain the pure *meso*- and *dl*-glycols[3,12] required for the preparation of the pure isomeric dibromides, this method should prove invaluable in synthesizing the *cis*- and *trans*-hexenes, heptenes, etc.

Work is now under way in this Laboratory on the preparation of the 3-hexenes and 3-heptenes from the corresponding glycols.

Experimental Part

***meso*- and *dl*-4,5-Octanediols.**—The pure *meso*- and *dl*-4,5-octanediols used in this work were prepared according to the method recently described.[12] The isomers had the

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[6] For a partial list of recent references on the preparation of olefins see: (a) Schmitt and Boord, THIS JOURNAL, **54**, 753 (1932); (b) Young and Lucas, *ibid.*, **52**, 1964 (1930); (c) Weston and Hass, *ibid.*, **54**, 3337 (1932); (d) Young and Winstein, *ibid.*, **58**, 102 (1936); (e) Whitmore and co-workers, *ibid.*, (1932–1933).

[7] (a) Wislicenus, Talbot, Henze and Schmidt, *Ann.*, **313**, 207 (1900); (b) Young, Dillon, Lucas, THIS JOURNAL, **51**, 2528 (1929); (c) Lauer and Stodola, *ibid.*, **56**, 1216 (1934); (d) Lucas and Prater, to be published soon.

[8] (a) Bourguel, *Bull. soc. chim.*, [4] **45**, 1067 (1929); (b) Bourguel and Gredy, *Compt. rend.*, **189**, 757 (1929); (c) Bourguel, Gredy and Piaux, *ibid.*, **195**, 129 (1932); (d) Gredy, *Bull. soc. chim.*, [5] **2**, 1029 (1935).

[9] Boord and co-workers, several papers in THIS JOURNAL (1930–1933).

[10] For example, see Soday and Boord, *ibid.*, **55**, 3293 (1933).

[11] (a) Farmer, Laroia, Switz and Thorpe, *J. Chem. Soc.*, 2937 (1927); (b) Kuhn and Winterstein, *Helv. Chim. Acta*, **9**, 87 (1928).

[12] Young, Levanas and Jasaitis, THIS JOURNAL, **58**, 2274 (1936).

following properties: *meso*-isomer, m. p. 123.5–124.5°; *dl*-isomer, m. p. 28°; b. p. (8 mm.) 109.8–110.0°; $n^{24.5}_D$ 1.4419.

The Reaction of Phosphorus Tribromide with the 4,5-Octanediols.—The most promising method of preparing the 4,5-dibromooctanes appeared to be the reaction of phosphorus tribromide on the dipropylglycols. However, when the general procedure described by Farmer and coworkers[11a] for the preparation of dibromohexadiene from divinylglycol was applied to the 4,5-octanediols, the yields were unsatisfactory.

Preparation of 4,5-Dibromooctanes, HBr–ZnBr$_2$ Method.—A mixture of 44 g. (0.3 mole) of *meso*-4,5-octanediol, 270 g. of 40% hydrobromic acid and 270 g. (1.2 moles) of zinc bromide contained in a 500-ml. round-bottomed flask was saturated with hydrogen bromide at 20°. The reaction mixture was allowed to stand overnight at this temperature. The flask was then attached to a reflux condenser and gradually warmed to 40° in a water-bath. This temperature was maintained during the day time over the next forty-eight to fifty-four hours but the flask was allowed to return to room temperature during the night. The dibromooctane, which gradually separated as an oil phase, amounted to 65–75% of the theoretical yield. At temperatures higher than 40° the reaction mixture had a tendency to become so dark that it was difficult to see the boundary between the dibromide and aqueous phases. The crude dibromide was then separated and washed several times with dilute sodium bicarbonate solution to neutralize the acid. The last washing was made with the bicarbonate solution since water occasionally formed a stable emulsion with the dibromide. The crude dibromide was then diluted with twice its volume of carbon tetrachloride and dried with anhydrous calcium chloride in the dark. Distillation of the dried solution through a 60-cm. Vigreux column gave 50 g. of dibromide, b. p. (4.5 mm.) 83–98°, n^{20}_D 1.4945. Per cent. bromine by Carius method, found: 58.24, 58.43; calcd.: for $C_8H_{16}Br_2$, 58.77. When the above method was used in preparing the dibromide from *dl*-4,5-octanediol, the reaction mixture became excessively colored and the yield of dibromooctane was less than half that obtained from the *meso*-glycol. Consequently, another procedure was adopted for preparing the dibromide from the *dl*-glycol (see HBr–diacetate method below).

Purification of *dl*-4,5-Dibromooctane from *meso*-4,5-Octanediol by the HBr–ZnBr$_2$ Method.—Since the dibromide obtained from the *meso*-4,5-octanediol described above had a boiling range of 15° and yet contained the required quantity of bromine for dibromooctane, it was at first thought to be a mixture of both the *dl*- and *meso*-dibromides. However, when it was treated with zinc in alcohol it gave a product which was approximately 50% unsaturated. (See discussion for explanation.) Consequently, several dibromide preparations were combined and purified as follows. The dibromide mixture was converted into a hydrocarbon mixture by the method of Gladstone and Tribe as modified by Wilkinson.[2] This hydrocarbon mixture was then placed in an all glass reaction flask kept at −15° and brominated by adding small amounts of bromine from time to time. At the end of the reaction, a slight excess of bromine was added to remove the last trace of unsaturated hydrocarbon. The product was washed immediately with dilute sodium bisulfite solution, sodium bicarbonate solution, and water, and then dried with anhydrous calcium chloride. Fractional distillation of the product at reduced pressures through a 70-cm. lagged, Vigreux column equipped with a Hopkins condenser in the Claisen-head gave crude octane, b. p. 123–125.5°, and *dl*-dibromooctane, b. p. (4.3 mm.) 84.3–85.8°. After further fractionation the *dl*-dibromooctane possessed the following properties: b. p. (4.3 mm.) 84.0–84.5°; d^{20}_4 1.4569; n^{20}_D 1.4981; MR found, 54.72; calcd. for $C_8H_{16}Br_2$, 54.38. Specific second order reaction rate constant with potassium iodide in methyl alcohol at 75°, $k_2 = 0.0996$. Per cent. bromine by Carius method, found, 58.46; calcd., 58.77.

Preparation of *meso*- and *dl*-Diacetoxyoctanes from *meso* and *dl*-4,5-Octanediols.—One-half mole quantities (73.0 g.) of either *meso*- or *dl*-4,5-octanediol, 2.5 moles (237 ml.) of acetic anhydride, and 1.5 moles (120 ml.) of pyridine were heated together under a reflux condenser at 85–95° for seven hours.[13] The mixture was then cooled, diluted with 600 ml. of water and saturated with sodium chloride. The upper layer which contained the diacetate was separated, diluted with an equal volume of ether and dried over anhydrous calcium chloride. After removal of the solvent the diacetate was fractionally distilled at reduced pressure through the column used in the distillation of the dibromooctanes. The yields of diacetates from both glycols averaged 75% of the theoretical. The products had the following properties: diacetate from *meso*-4,5-octanediol, b. p. (5.0 mm.) 100°; n^{20}_D 1.4252; d^{20}_4 0.9686; MR found, 60.89; calcd. for $C_{12}H_{22}O_4$, 60.84; equivalent weight, found: 114.5; calcd., 115.1; diacetate from *dl*-4,5-octanediol, b. p. (5.5 mm.) 110°; m. p. 26°; n^{20}_D 1.4283; d^{20}_4 0.9732; MR found, 60.88; calcd., 60.84; equivalent weight, found, 115.6; calcd., 115.1.

Preparation of 4,5-Dibromooctanes, HBr–Diacetate Method.—Three-tenths of a mole (69.0 g.) of the diacetate from either *meso*- or *dl*-4,5-octanediol and 210 g. of 48% hydrobromic acid were placed in a 500-ml. glass-stoppered bottle and the mixture was saturated with hydrogen bromide at 0°. After the glass stopper was wired on, the bottle was placed in an ice box. After ten days the oil phase which formed was separated, washed, dried, distilled and purified as described above for the dibromide from the HBr–ZnBr$_2$ method. The yields of dibromooctanes from both of the diacetates averaged 55% of the theoretical before the final purification, in which there was usually a 90–95% recovery. The properties of the *meso*-4,5-dibromooctane obtained from the diacetate from the *dl*-4,5-octanediol are as follows: b. p. (4.3 mm.) 79–80.0°; n^{24}_D 1.4967; d^{20}_4 1.4525; MR found, 54.94; calcd. for $C_8H_{16}Br_2$, 54.38. Specific second order reaction rate constant with potassium iodide in methyl alcohol at 75°, $k_2 = 0.127$. Bromine by Carius method, found, 58.64; calcd., 58.77%.

Preparation of the *cis*- and *trans*-4-Octenes

(a) The Reaction of Phosphorus Triiodide with *meso*-4,5-octanediol.—Since phosphorus triiodide was used ef-

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[13] This procedure was adopted with the idea of obtaining good yields of a product free from the mono-acetate. Since the results were entirely satisfactory it was used throughout the work. It is possible that smaller quantities of acetic anhydride and a shorter period of heating would be just as acceptable.

fectively in the preparation of the diphenyl polyenes by Kuhn and Winterstein,[11b] this reagent, prepared from yellow phosphorus and iodine in carbon disulfide, was allowed to react with *meso*-4,5-octanediol (0.1 mole) according to their directions. The reaction mixture was then poured onto ice and the carbon disulfide layer was washed with dilute sodium thiosulfate solution, dilute sodium bicarbonate solution, and water, and dried over anhydrous calcium chloride. Distillation of the dried solution through a 60-cm. Vigreux column gave 6.3 g. of product, b. p. (47 mm.) 112–114°. This product did not react with bromine. It evolved iodine, however, when exposed to the light but not when heated at 75° for several hours. Molecular weight by Beckmann method in benzene, found, 240; calcd. for $C_8H_{17}I$, 240.1. It was therefore concluded that the product was probably 4-iodooctane formed by partial reduction. No further identification was made. There was no evidence for the formation of 4-octene by this method.

(b) **The Reaction of 4,5-Dibromooctane with Potassium Iodide in Aqueous Acetone at 75°.**—A mixture of 27.2 g. (0.1 mole) of dibromooctane from the HBr–$ZnBr_2$ method, and 40 ml. of saturated potassium iodide solution was made up to a volume of 250 ml. with acetone and sealed in a 500-ml. glass bulb. The bulb was placed in a thermostat at 75°. Every twelve hours the bulb was cooled rapidly to room temperature and opened. A 5-ml. portion of the reaction mixture was titrated against standard sodium thiosulfate solution and the bulb was resealed and placed in the thermostat again. After forty-eight hours the iodine concentration became constant. The yield of octene based on the iodine liberated was calculated to be 55.5%. It was concluded that this poor yield resulted from the establishment of an equilibrium between diiodooctane, iodine and octene and the method was discarded in favor of the zinc–copper couple method of preparing octene. However, since it was found later that the dibromooctane used in this work was actually a mixture of approximately equal quantities of 4,5-dibromooctane and of 4,4-dibromooctane which would not be expected to liberate iodine with potassium iodide, it is evident that the reaction to form octene actually went to completion and the method described above would be just as acceptable for the preparation of octene as the zinc–copper couple method.

(c) **The Reaction of *meso*- and *dl*-4,5-Dibromooctane with Zinc–Copper Couple in Alcohol.**—*cis* and *trans*-4-octenes were prepared from the pure *dl*- and *meso*-4,5-dibromooctanes by the method of Gladstone and Tribe as modified by Wilkinson.[2] After distillation at reduced pressure the octenes possessed the following properties:[14] *cis*-4-octene from *dl*-dibromooctane, m. p., approx. −115°; b. p. (97.4 mm.) 61.9°; b. p. (760 mm.) 20–20.5°; $n^{24.2}D$ 1.4111; d^{20}_4 0.7186; MR found, 38.92; calcd., 38.46. Analysis for unsaturation, 100.5% *trans*-4-octene from *meso*-dibromooctane, m. p. approx. −105°; b. p. (103 mm.) 62.9 mm.; b. p. (760 mm.) 20–20.5°; $n^{24.2}D$ 1.4110; d^{20}_4 0.7165; MR found, 39.03_4; calcd., 38.46. Analysis for unsaturation, 99.7%.

The authors are indebted to Dr. G. Ross Robertson of this Laboratory and Professor H. J. Lucas of the California Institute of Technology for their helpful suggestions.

Summary

1. *cis* and *trans*-4-octenes have been prepared from *dl*- and *meso*-4,5-dibromooctanes by the action of zinc–copper couple in alcohol. The direct action of phosphorus triiodide on *meso*-4,5-octanediol gives a monoiodooctane instead of the expected octene.

2. *meso*- and *dl*-4,5-dibromooctanes have been prepared: (a) from *meso*- and *dl*-4,5-octanediols by the action of a solution of zinc bromide, saturated with hydrogen bromide at 20°, on the glycols and (b) by the action of hydrobromic acid, saturated at 0°, on the 4,5-diacetoxyoctanes from the *meso*- and *dl*-4,5-octanediols.

3. A change of configuration occurs during the conversion of the glycols into the dibromooctanes. The *meso*-4,5-octanediol gives *dl*-4,5-dibromooctane and the *dl*-4,5-octanediol gives *meso*-4,5-dibromooctane.

4. 4,4-Dibromooctane is also formed from the *meso*-4,5-octanediol by the HBr–$ZnBr_2$ reagent, due to a pinacolone rearrangement.

5. The synthesis of the normal *cis–trans*-alkenes has been discussed.

LOS ANGELES, CALIF. RECEIVED DECEMBER 14, 1936

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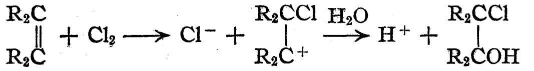
[14] The approximate melting points of the 4-octenes were obtained through the kindness of Mr. Saul Winstein, a graduate student at the California Institute of Technology. Due to the fact that the necessary equipment was not available, the exact melting points of the octenes have not yet been determined.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Mechanism of Addition Reactions. Chloro- and Bromo-Beta-Lactones from Dimethylmaleic and Dimethylfumaric Acids

BY D. STANLEY TARBELL AND PAUL D. BARTLETT

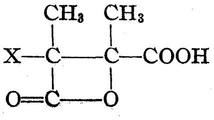
Recent kinetic evidence on the bromination of stilbene in methyl alcoholic solution[1] has by analogy strengthened the view that the following steps are involved in the formation of chlorohydrins in aqueous solution



$$\begin{matrix}R_2C\\ \| \\ R_2C\end{matrix} + Cl_2 \longrightarrow Cl^- + \begin{matrix}R_2CCl\\ | \\ R_2C^+\end{matrix} \xrightarrow{H_2O} H^+ + \begin{matrix}R_2CCl\\ | \\ R_2COH\end{matrix}$$

where the first and second steps may or may not occur synchronously. We have investigated the aqueous chlorination and bromination of dimethylmaleic and dimethylfumaric acids in the search for more detailed information about this process.

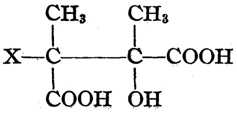
When the sodium salt of dimethylmaleic acid is treated with chlorine water or bromine water, there can be isolated in poor yield from the resulting oil a halogenated beta-lactone (I or II),



I X = Cl, m. p. 92–94°

II X = Br, m. p. 95–96°

whose structure is established by analysis, neutralization equivalent and molecular weight determinations. Several hours of standing in 5% sulfuric acid at room temperature opens the lactone ring irreversibly to the halohydrin acid (III or IV). This accounts for the small amounts of halohydrin acid which appear occasionally along with the lactones when these have been allowed to stand in solution before isolation.



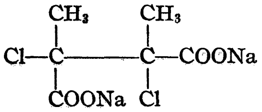
$$\begin{array}{ccc} & CH_3 & CH_3 \\ & | & | \\ X- & C- & C-COOH \\ & | & | \\ & COOH & OH \end{array}$$

III X = Cl, m. p. 171–173°

IV X = Br, m. p. 168–170°

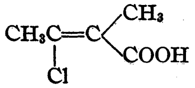
The reaction of sodium dimethylfumarate with chlorine water or bromine water takes an exactly similar course, leading to a pair of beta-lactones (V, m. p. 141–142°, and VI, m. p. 148–150°) which are stereoisomeric with I and II. Acid hydrolysis opens these lactones to the same chlorohydrin and bromohydrin, respectively, (III and IV) as are obtained from the lactones of the maleic series. Since these halohydrin acids melt with decomposition, a check on the stereochemical purity and identity of the chlorohydrins was obtained by measuring the rate of their reaction with aqueous sodium hydroxide, a type of process whose rate in the unmethylated series[2] is very dependent upon configuration. Both I and V yielded samples of III which reacted as a single substance with sodium hydroxide, and both at the same rate, within the experimental accuracy. This test was not applied to the bromohydrin acids.

The beta-lactones cannot be made from the halohydrins; therefore if any *one-step addition* (of chlorine or hypochlorous acid) preceded the formation of the chlorolactone in solution, it must have been the addition of chlorine to give a symmetrical sodium dichlorodimethylsuccinate (VII) which might then eliminate sodium chloride to form the lactone. Only one of the two possible acids of this structure is known,[3] but since both lactones have been prepared, the known acid should give one of them if a dichloro acid is intermediate at all in this process. It was found, as expected from previous work,[4] that when this acid was neutralized with sodium bicarbonate and allowed to stand at room temperature for two days, there was produced chlorotiglic acid (VIII), m. p. 66–68°, some of the starting material still remaining unchanged, and no beta-lactone appearing. A quantitative run on the elimination of sodium chloride from VII showed that this reaction requires about twenty-four hours at 25°, while both lactones have been isolated in less than half an hour from the reaction mixture. Therefore the dichloro acid is not intermediate in the formation of the lactone, which is instead the product of a two-step addition process.



$$\begin{array}{ccc} & CH_3 & CH_3 \\ & | & | \\ Cl- & C- & C-COONa \\ & | & | \\ & COONa & Cl \end{array}$$

VII



VIII

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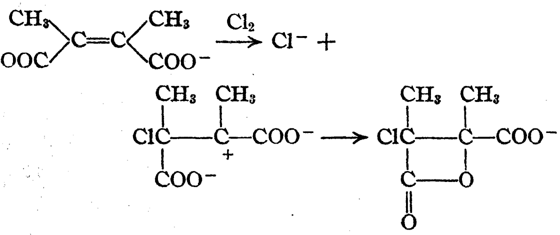
[1] Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

[2] Kuhn and Ebel, *Ber.*, **58**, 919 (1925).

[3] Michael, *J. prakt. Chem.*, [2] **46**, 382 (1892).

[4] Otto and Beckurts, *Ber.*, **18**, 847 (1885); Otto and Holst, *J. prakt. Chem.*, **149**, 467 (1890).

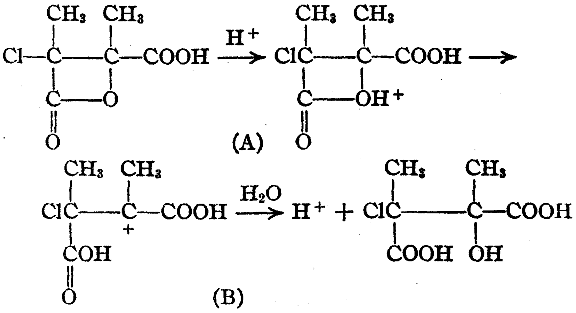
The most likely such process, in view of the evidence in the case of analogous reactions, is



These steps may be pictured as occurring in succession, or synchronously. Against the idea of successive reaction steps stands the unlikelihood that the intermediate zwitterion could long survive without a stereochemical equilibration which would lead to identical products from both dimethylmaleic and dimethylfumaric acids. On the other hand, the idea of a simultaneous attack of halogen and carboxylate oxygen upon the ends of the double bond places us immediately in stereochemical difficulties; for a model of the molecule in question shows that either a methyl or a carboxylate group directly confronts the attacking oxygen in the fumarate or maleate ion, and very large torsion of the rigid double bond structure would be necessary if this attack occurred *before* the complete opening of the double bond by the halogen. These difficulties are best avoided by the hypothesis that the reaction steps occur in the quickest possible succession.

Two other well-known puzzling facts of organic chemistry are reëmphasized in this series. One is the total inertness of the completely substituted ethylene, dimethylmaleic anhydride, toward bromine, described below. The other is the great effect of methyl substitution in favoring ring-closure. Free dimethylmaleic acid is completely unknown, the spontaneous formation of its anhydride being very rapid under all experimental conditions; the appearance of beta-lactones on halogenation of its salts is another manifestation of the enhancement of ring closure by methyl groups. Probably a satisfactory explanation of these effects of methyl substitution, and of the course of the halogenlactone formation, can be found only at the same source.

The formation of a common chlorohydrin acid from the two isomeric chlorolactones makes it clear that the ring-opening of these lactones by 5% sulfuric acid is not an ordinary ester hydrolysis, a process which occurs without stereochemical inversion at the alcoholic hydroxyl group. Models show so little difference in the apparent availability of the lactonic carbonyl groups of the two isomers to attack, that we propose that *neither* ring-opening is a normal ester hydrolysis, but that the opening occurs according to the mechanism



Here the exchange reaction between the positive ion (B) and water is assumed to be slow enough to permit the positive ion (B) to take up its preferred configuration before reaction. Thus in the lactone *formation* the presence of an active negative ion near the positive carbonium center makes reaction faster than steric equilibration; under the acid conditions of hydrolysis the intermediate must react with a neutral molecule (water), and the reverse is true.

The hydrolysis of the lactones under alkaline conditions would have been interesting from this point of view, but it was attended by replacement of the halogen and led to no isolable compounds. From treatment of the chlorohydrin with barium hydroxide at 0° a small amount of material was obtained, m. p. 158–160° with decomposition, which gave analytical figures for the oxidic acid, 2,3-epoxybutane-2,3-dicarboxylic acid. That no hydroxylactone was formed in this reaction was shown by a rate run in which the amount of chloride ion produced was always equal to that of hydroxyl ion consumed. When the sodium salt of the chlorolactone (I) was heated in aqueous solution on the steam-bath, chlorotiglic acid was produced; similar treatment of the isomeric chlorolactone salt yielded a solid mixture melting at 180–240°, which was not studied further.

In agreement with Michael,[3] we were unable to obtain a bromine addition product from dimethylmaleic anhydride in carbon tetrachloride solution. Illumination with a 400-watt projection lamp discharged the bromine color in a few minutes, but hydrogen bromide was evolved copiously, and the starting material was the only solid obtainable from the solution. Only the bromohydrin acid resulted from treatment of the bromolactone II with 40% hydrobromic acid. Equivalent quantities of dimethylmaleic anhydride and bromine stood for three weeks in glacial acetic acid 1 *N* in hydrogen bromide (catalytic conditions, in the experience of Williams and James[5]) without visible reaction.

Experimental

Preparation of Dimethylmaleic Anhydride.—Acetoacetic ester was methylated with methyl bromide, the bisulfite derivative of the methylated ester treated with sodium cyanide, the nitrile hydrolyzed and the resulting dimethylmaleic acid dehydrated, according to the procedure of Ott,[6] with an over-all yield of 19.5%.

Bromination of Dimethylmaleic Acid.—Twenty-five grams of dimethylmaleic anhydride was neutralized with 16 g. of sodium hydroxide in 200 cc. of water, and added to a solution of 32 g. of bromine in 2 liters of water. Reaction was complete in a few minutes. The solution was extracted three times with ether, then acidified with 0.2 equivalent of sulfuric acid and extracted three times more. The ether was evaporated, yielding 38.3 g. of mixed oil and crystals. After four crystallizations from benzene–petroleum ether, there resulted 5.3 g. (11%) of bromohydrin acid, m. p. 155–160°, and 14.8 g. of pure lactone (33%), m. p. 95–96°, crystallizing in clumps of thick needles. The presence of ether interferes with crystallization of the lactone. It is very soluble in the common solvents, except petroleum ether.

Anal.[7] Calcd. for $C_6H_7O_4Br$: C, 32.3; H, 3.2; Br, 35.83. Found: C, 32.3; H, 3.4; Br, 36.37, 35.10. Molecular weight calculated, 223; found in benzene, 422; in acetic acid, 197, 192. Equivalent weight by titration with alkali in the cold, 205; in hot water, 85.4, indicating that the ring has been opened and the bromine removed.

In the presence of much bromide ion no dibromo acid was isolated, but only the lactone. Five grams of anhydride, 3.2 g. of sodium hydroxide, and 6.4 g. of bromine reacted in 25 cc. of water containing 10 g. of sodium bromide; 2.7 g. (30%) of lactone, m. p. 80–90°, was obtained, and the only other product in evidence was a soluble lachrymator.

Action of Acids on the Bromolactone.—One gram of bromolactone was dissolved in 50 cc. of 10% sulfuric acid and let stand overnight at room temperature; a white solid, melting with decomposition at 168–170°, was obtained, which was recrystallized from chloroform. It is soluble in water, ether, acetone, ethyl acetate, slightly soluble in chloroform, and almost insoluble in benzene. It is best recrystallized from ethyl acetate–chloroform, or ethyl acetate–benzene.

Anal. Calcd. for $C_6H_9O_5Br$: C, 29.9; H, 4.1. Found: C, 29.8, 29.9; H, 4.2, 4.1.

To find out whether the bromohydrin acid isolated in the bromination of dimethylmaleic acid was formed from the lactone, a rough rate run was carried out by dissolving 1.0 g. of lactone in 50 cc. of 5% sulfuric acid, and determining the melting points of samples extracted at intervals.

Time	M. p., °C.
15 min.	60– 80
71 min.	80–100
220 min.	130–145
20 hrs.	166–169

It appears that the reaction is fairly complete at four hours, and hence the bromohydrin and chlorohydrin acids are considered secondary products.

Chlorination of Dimethylmaleic Acid.—Five grams of the anhydride was neutralized with 3.2 g. of sodium hydroxide in 100 cc. of water, and chlorine passed in until the presence of an excess was shown by a test with potassium iodide paper. Isolation and fractional crystallization of the product in the same manner as for the bromolactone gave 0.55 g. of chlorohydrin acid (7%), m. p. 150–168°, and 2.9 g. (41%) of chlorolactone, m. p. 80–90°. The best sample of this lactone obtained melted at 92–94°. The chlorolactone has the same solubility properties and general crystalline form as the bromolactone.

Anal. Calcd. for $C_6H_7O_4Cl$: C, 40.3; H, 4.0; mol. wt., 178.5. Found: C, 39.9, 40.0, 40.0; H, 4.7, 4.5, 4.8; mol. wt. in glacial acetic acid, 158.

Hydrolysis of the Chlorolactone I.—One gram of the chlorolactone was dissolved in 50 cc. of 10% sulfuric acid and let stand overnight at room temperature. Extraction and crystallization of the product from ethyl acetate–benzene gave a substance which decomposed at 173–174° when heated from 150° at 5° per minute. The solubility properties are similar to those of the bromohydrin.

Anal. Calcd. for $C_6H_9O_5Cl$: C, 36.6; H, 4.6. Found: C, 36.6; H, 4.9.

The chlorohydrin acid was also prepared in 62% yield from dimethylmaleic anhydride by conducting the hydrolysis without isolation of the chlorolactone.

Formation of the Oxidic Acid.—Two grams of the chlorohydrin acid was dissolved in 50 cc. of water, treated with 4.7 g. of barium hydroxide, and kept overnight at 0°. The solution was neutral in the morning. It was evaporated under diminished pressure over a period of several days and 1.4 g. of barium salt filtered off. This was suspended in water and acidified with 10 cc. of 1 *N* hydrochloric acid. From the ether extract a small amount of white compound crystallized, which gave no Beilstein test. Recrystallized from ethyl acetate–benzene, it melted at 158–160° with decomposition.

Anal. Calcd. for $C_6H_8O_5$: C, 45.0; H, 5.0. Found: C, 44.7; H, 5.3.

Reaction Rate of Chlorohydrin Acid with Sodium Hydroxide.—1.010 g. of chlorohydrin acid was dissolved in water and made up to 100 cc. Fifty cubic centimeters of this solution, cooled to 0°, was added to a solution of 300 cc. of water and 85.94 cc. of 0.0973 *N* sodium hydroxide at the same temperature. This was 25% excess alkali over that required to produce the sodium salt of the oxidic acid. Parallel 25-cc. samples were pipetted out at intervals and titrated for hydroxyl ion and chloride ion, respectively. The Cl^- ion produced was equal, within a few per cent., to the OH^- ion consumed, throughout the reaction. The relationship between time and log $(OH^-)/(\text{chlorohydrin})$ is linear, and from it we obtain the rate constant for the bi-

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[5] Williams and James, *J. Chem. Soc.*, 343 (1928).

[6] Ott, *Ber.*, **61**, 2131 (1928).

[7] These three analyses were carried out by Mrs. G. M. Wellwood.

molecular reaction 0.163 (time in minutes, concentration in moles per liter).

Time	OH^- consumed	Cl^- produced
250	0.00126	0.00134
885	.00299	.00310
1095	.00331	.00347
1480	.00392	.00398
2365	.00457	.00468
2725	.00466	.00489

Preparation of Dimethylfumaric Acid.—This was accomplished by the method of Ott;[8] a high pressure hydrogenation bomb served as the reaction vessel. Sodium dimethylmaleate is heated in aqueous solution for two days at 185–190°. Acidification and extraction yields a mixture of dimethylmaleic anhydride, dimethylfumaric acid and methylitaconic acid, which can be separated by crystallization from chloroform, in which only the dimethylfumaric acid is insoluble. This is recrystallized from water, and melts at 245°. It was obtained in 37% yield, 7.5% of methylitaconic acid being obtained and 41% of dimethylmaleic anhydride recovered from the same run.

The bromination and chlorination of dimethylfumaric acid were carried out in the same manner as for dimethylmaleic acid, but speed in isolation was especially necessary in order to forestall hydrolysis of the halogen lactones to halohydrin acids. These halogen lactones are higher melting than their isomers and are advantageously crystallized from chloroform.

The bromolactone from dimethylfumaric acid was obtained melting at 148–150°, crystallizing in white rods from chloroform. When titrated in the cold with sodium hydroxide to phenolphthalein, it showed an equivalent weight of 185, compared to 223 calculated. The end-point drifted rather rapidly.

Anal. Calcd. for $C_6H_7O_4Br$: C, 32.3; H, 3.2. Found: C, 32.0; H, 3.4.

The Chlorolactone from Dimethylfumaric Acid.—Twelve grams of dimethylfumaric acid yielded, after two fractional crystallizations of the product, 0.4 g. of starting material, 3.0 g. of chlorohydrin acid, m. p. 155–160° (18.3%), 4.1 g. of lactone, m. p. 138–140° (27.5%), and 1.6 g. of lower-melting fractions. The best sample obtained melted at 141–142° without decomposition. It is soluble in water and the common organic solvents, and crystallizes from benzene in typical rosets of needles.

Anal. Calcd. for $C_6H_7O_4Cl$: C, 40.3; H, 4.0; mol. wt., 179. Found: C, 40.0, 40.2; H, 4.3, 4.4; mol. wt. by titration in the cold, 160; in hot water, 65.5.

The identity of the chlorohydrin acid obtained from dimethylfumaric acid with that obtained from dimethylmaleic acid could not be established by mixed melting points, since this compound melts with decomposition. Therefore a pure sample obtained from dimethylfumaric acid was characterized by the rate of its reaction with sodium hydroxide at 0°, in the same manner as described for the sample from dimethylmaleic acid. The bimolecular rate constant obtained in the present instance was 0.152 compared with 0.163 in the other case. This difference is within the experimental error.

Experiments with *sym*-Dimethyldichlorosuccinic Acid.—The acid was prepared by the method of Michael[3] and after recrystallization from benzene–ether melted at 182–184° with decomposition. One gram was neutralized with sodium carbonate in 50 cc. of water and let stand for two days at room temperature. Acidification and extraction, followed by fractional crystallization from benzene, yielded starting material and chlorotiglic acid, m. p. 66–68°.

The rate of elimination of sodium chloride from sodium dimethyldichlorosuccinate was determined by making 100 cc. of an aqueous stock solution containing 0.4805 g. of the free acid. Fifty cubic centimeters of this solution was neutralized by 22.66 cc. of 0.0973 *N* alkali and kept at 25° in a thermostat. Ten cubic centimeter samples were titrated for chloride ion at intervals with silver nitrate.

Time, min.	30	105	1065	2505
Titer	0.48	0.88	4.96	7.91
% reaction	6	12	66	105

Both chlorolactones have been isolated in less than thirty minutes, so the salt of the dichloro acid does not decompose fast enough to account for the formation of either lactone.

Summary

1. The chlorination or bromination of sodium dimethylmaleate and dimethylfumarate in aqueous solution yields stereoisomeric chloro- or bromo-beta-lactones as the primary products of reaction.

2. The isomeric chlorolactones are readily hydrolyzed irreversibly to a single chlorohydrin acid, and the isomeric bromolactones to a single bromohydrin acid.

3. It is shown that these facts are inconsistent with a mechanism of addition of halogen in a single step, and the probable mechanisms of these reactions are briefly discussed.

4. Conclusions previously reached on the basis of kinetic results are now confirmed by preparative evidence.

CAMBRIDGE, MASS. RECEIVED DECEMBER 14, 1936

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[8] Ott, *Ber.*, **61**, 2131 (1928). *Cf.* also Fittig, *Ann.*, **304**, 158 (1899), and Lutz and Taylor, THIS JOURNAL, **55**, 1589 (1933).

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

Studies in the Oxidation of Alpha Ray Cuprene[1]

BY S. C. LIND[2] AND C. H. SCHIFLETT[3]

Acetylene under alpha-radiation from radon yields a yellow solid polymer of acetylene, cuprene. The yield per ion pair is approximately twenty molecules.[4] The product is unusually inert to ordinary reagents, and no satisfactory solvent has been found by means of which a molecular weight determination can be made.

Analysis by combustion of the freshly prepared product and of the gas phase indicates the product to be almost an exact polymer. The following is a typical analysis of the solid: C, 90.5%; H, 7.52%; diff., 1.98%; C:H ratio 12.03. The theoretical C:H ratio is 11.80. This 1.98% difference is very probably due to reaction with oxygen of the air, as some ten minutes were required for obtaining and weighing the sample for analysis, during which time the product was open to the air. (It will be shown later that oxidation proceeds rapidly when the product is first exposed to oxygen.) The discrepancy between the experimental and theoretical C:H ratio (for a true polymer) is no doubt due to loss of hydrogen which previously has been shown to accompany the reaction.[5]

In view of the fact that in most instances at any rate the substance under investigation was not the original condensation product but an oxidized product, it was considered worth while to determine whether the freshly prepared unoxidized substance possessed the same indifference toward solvents as had been found for the oxidized substance. Accordingly a sample of the freshly polymerized cuprene was opened in an atmosphere of acetylene and portions treated with the following in the hope of effecting solution for a molecular weight determination: water, ethyl alcohol, ether, acetone, carbon disulfide, carbon tetrachloride, benzene. After a period of twenty-four hours with frequent shaking none had dissolved in any of these liquids.

Many previous attempts[6] have been made to determine the constitution of cuprene (prepared by electrical discharge, or by the catalytic effect of copper), and although it was known that oxygen was absorbed rapidly from the air, apparently many of these investigations were made not only in the presence of air but after the substance had been exposed to air for some time. Losanitsch[7] reported much difficulty in analysis of the polymer due to rapid absorption of oxygen from the air. Jovitschitsch[8] found a 22% deficiency on analysis by combustion and claims to have excluded the possibility of oxidation from the air by working rapidly. He also found no difference in two samples, one analyzed immediately, the other after long standing in the air. However, this is entirely out of agreement with other workers.

From the C:H ratio in the above analysis one calculates that hydrogen is liberated to the extent of approximately 1% of the total acetylene polymerized. By manometric measurements during the course of reaction it was found (*loc. cit.*) that this per cent. ranges from about 0.7% at the beginning to several per cent. at the end, averaging about 2% over the entire course of the polymerization.

It was found that this product oxidizes spontaneously at room temperature, and the present study was undertaken with a view to determine the rate and extent of the oxidation. The oxidation has been followed both manometrically and gravimetrically. The products were analyzed with the results given elsewhere in this paper.

Experiment No. 1.—Cuprene was prepared in a 524-cc. flask from acetylene at a pressure maintained at approximately one atmosphere, by admission of the gas at various intervals. Radon was mixed with the acetylene. After eleven days, when the radon had decayed to approximately 14% of its original amount, the vessel was evacuated thoroughly. Oxygen at 682.3 mm. pressure (S. T.) was then admitted and the pressure was read at intervals. The manometric data are plotted in Fig. 1.

The oxidized product from the above reaction was then

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(1) This work was supported in part by a grant from the Fluid Research Fund of the Graduate School, University of Minnesota.

(2) Director of the School of Chemistry, University of Minnesota.

(3) Assistant Professor of Chemistry, Macalester College, St. Paul, Minnesota.

(4) Lind and Bardwell, *Science*, **62**, 422 (1925); Mund and Koch, *J. Phys. Chem.*, **30**, 293 (1926).

(5) Lind, "Chemical Effects of Alpha Particles," A. C. S. Monograph, Chemical Catalog Co., New York, 1928.

(6) Walter Herzog, *Kunstoffe*, **21**, 49–53 (1931); Kaufmann and Mohnhaupt, *Ber.*, **56B**, 2533 (1923); Sabatier and Senderens, *Compt. rend.*, **130**, 250 (1900).

(7) S. M. Losanitsch, *Ber.*, **40**, 4656 (1907).

(8) M. Z. Jovitschitsch, *Monatsh.*, **29**, 5–14 (1907).

removed from the reaction vessel, a sample was taken for combustion analysis and the remainder weighed and kept in a desiccator, open to the air. Over a period of eighteen months the product showed no further gain in weight. The analysis of the product was: C, 68.8%; H, 5.90%; diff., 25.3%; C:H ratio 11.69.

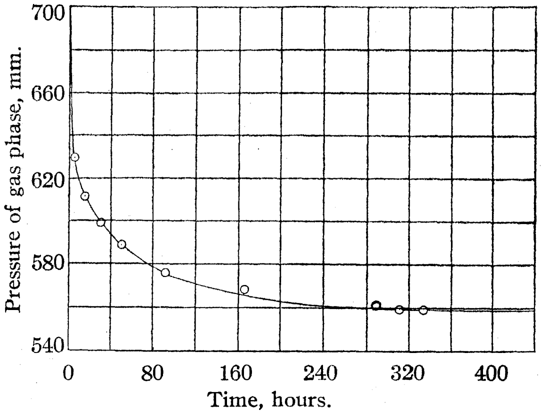

Fig. 1.—Oxidation of cuprene followed manometrically.

In another experiment cuprene was prepared in the same manner as given above and opened to desiccated air for a period of three and one-half months, when it was analyzed with the following results: C, 69.3%; H, 5.91%; diff., 24.75%; C:H ratio 11.65.

Experiment No. 2.—In another experiment, the freshly prepared cuprene was removed from the reaction vessel and weighed as quickly as possible. It was then kept exposed to desiccated air and weighed at intervals. The results are shown in Fig. 2. After six and one-half months this product was analyzed as follows: C, 67.51%; H, 5.59%; diff., 26.9%; C:H ratio 12.08.

Experiment No. 3.—In a 215.15-cc. vessel, 0.1609 g. (0.00619 mole) of acetylene was polymerized in the usual manner and the remainder of the gas was pumped off. Oxygen was then introduced. After eleven days and five and one-half hours, a decrease in pressure, corrected to S. T., of 85.8 mm. was observed. The remaining gas, 273.0 mm. (S. T.), was then pumped out by means of a Toepler pump through two traps, the first surrounded by solid carbon dioxide–acetone and the second by liquid air and then into a receiver for analysis of the gas. Upon removal of the liquid air a pressure rise of 2.3 mm. at 24.8 was observed, less than 1% of the total. Upon removal of the solid carbon dioxide–acetone bath a pressure rise of 2.1 mm. at 24.8 was observed. The average of a series of semi-micro analyses shows the gas remaining after oxidation is complete to consist of traces of carbon dioxide, water vapor, 7.13% carbon monoxide and 92.85% oxygen. Reduced to standard conditions this amounts to 5.4 cc. of carbon monoxide and 71.7 cc. of oxygen. From the total amount of oxygen originally introduced, 101.6 cc., and the amount remaining, 71.7 cc., the amount of oxygen reacting is seen to be 29.9 cc. This is approximately five and one-half times the volume of carbon monoxide formed. The following chemical equation accounts for these results: $(C_2H_2)_{20} + 5^1/_2O_2 \longrightarrow C_{39}H_{40}O_{10} + CO$. The percentage composition of the above formula is: C, 70.1; H, 6.0; O, 23.9; C:H ratio, 11.67. This is in fair agreement with the data obtained by combustion analysis of the oxidized product.

Before the production of carbon monoxide was established definitely it was proposed that this process might consist simply of adsorption, and to clear up this point the oxidized product was heated in an evacuated vessel to 200°, at which temperature charring and decomposition with the distillation of a brown, oily liquid began to occur. Up to approximately 200° no pressure of gas was developed and no obvious change occurred.

Heats of combustion of the unoxidized and the oxidized cuprene, respectively, were determined and found to be as follows:

	Cal./gram	Cal./mole
Unoxidized cuprene	10,203.7	265,296.2
Oxidized cuprene	7,113.5	184,951.0

These values are 85.6 and 59.4%, respectively, of 312,000 cal./mole, which is the value given for the heat of combustion of acetylene in the literature.[10] It was found necessary to pellet these materials with about ten times their weight of sugar for these determinations in order to secure complete combustion. The ignition in the oxygen bomb of cuprene itself and even too rich mixtures of cuprene with sugar resulted in explosion and consequent scattering of the material in the bomb. The value of the heat of combustion of the unoxidized cuprene given above when compared with that of acetylene indicates clearly that the polymerization process is an exothermic one, and is consistent with the conclusions of Heisig.[11] The difference in the heats of combustion of acetylene and of the polymer gives at once the heat of polymerization, *viz.*, ap-

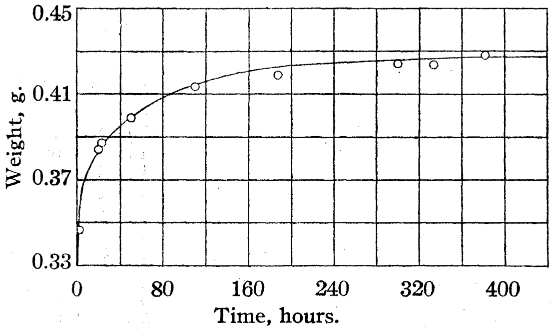

Fig. 2.—Oxidation of cuprene followed gravimetrically.

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(9) It should be pointed out in connection with the above chemical equation proposed to account for the analysis of solid and gaseous products and the manometric data that other equations will account for the facts almost equally well. For example

$$(C_2H_2)_{24} + 6^1/_2O_2 \longrightarrow C_{47}H_{48}O_{12} + CO$$

would give a net pressure drop only 2 mm. greater than the equation proposed above. The solid would analyze: C, 70.2; N, 6.02; O, 23.78; C:H ratio 11.67, which is nearly as satisfactory as the other. The difference in the gas analysis would also be well within the limits of error. However, it seems quite certain that these equations tell in general the nature of the reaction, *viz.*, that some polymer of acetylene of the order of 20 molecules reacts with oxygen to a definite compound and that in this oxidation carbon is eliminated with the formation of a small amount of carbon monoxide.

(10) I. C. T., McG.-H. Pub. Co., 1929, Vol. V, p. 163.

(11) G. B. Heisig, *J. Phys. Chem.*, **36**, 1000–1005 (1932).

proximately 47 kcal. per molecule of acetylene condensed. Calculating the theoretical heat of polymerization from the values of atomic linkages given by Fajans,[12] on the assumption that in the polymerization one C≡C (161.6 kcal.) is broken and one C=C (122.9 kcal.) and one C—C (73.5 kcal.) are formed per molecule of acetylene, one obtains the value 35 kcal. This is not in too good agreement with the experimental value to be sure, but perhaps as satisfactory as one could expect when it is remembered that the atomic linkages are admittedly only average values.

Acknowledgments.—We wish to thank Dr. F. H. Stodola, to whom we are indebted for the analyses of the solid products, and to acknowledge the kindness of Professor A. E. Stoppel who collaborated with us in determining the heats of combustion.

Summary

Cuprene was prepared by polymerization of acetylene by means of radon mixed with the gas. The solid polymer was then exposed to oxygen and the spontaneous reaction with oxygen at room temperature was followed manometrically. Both the solid and gaseous products were analyzed. The solid product after oxidation (which is nearly complete in twelve or fifteen days) contains approximately 25% oxygen. A little carbon monoxide is formed. The complete analysis shows the following reaction equation to be approximately correct

$$(C_2H_2)_{20} + 5^1/_2O_2 \longrightarrow C_{39}H_{40}O_{10} + CO$$

The spontaneous oxidation was also followed gravimetrically by exposing the freshly prepared cuprene to dry air and weighing at intervals. The results agree with the manometric method and analysis both as to extent and rate of oxidation. The heat of combustion of the oxidized cuprene is approximately 30% less than that of the unoxidized cuprene.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 10, 1936

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[12] Fajans, *Ber.*, **53**, 643 (1920); Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., Inc., New York, 1931, p. 323.

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF MINNESOTA]

A Catalytic Method for Determination of Iodine

BY HAROLD P. LUNDGREN[1]

Among the methods used for determination of iodine there are: those determining iodine colorimetrically in a solvent, those titrating iodine using the blue starch–iodine complex as an indicator, those employing a color or precipitation reaction of iodine and those employing the catalytic power of iodine.

It is often necessary to analyze for iodine in concentrations too low to be detected by ordinary colorimetric, volumetric or gravimetric technique. The concentration of iodine may be increased by the Winkler technique until it is within the analytical range. The success of the Winkler method depends on how far the reactions concerned go toward completion. Furthermore, any trace of oxidizing agent left in the solution will cause serious error.

The catalytic methods for determination of iodine are in many cases sensitive to microgram quantities of iodine and are relatively simple and accurate procedures. Bredig and Walton[2] utilized the catalytic activity of iodine in the decomposition of hydrogen peroxide; Bobtelsky and Kaplan[3] utilized the rate of decoloration of permanganate by oxalic acid as catalyzed by iodine. Baines[4] employed the catalytic effect of iodine on the oxidation of thiosulfate by nitrite. Sandell and Kolthoff[5] made use of iodine catalysis in the oxidation of arsenous acid by ceric sulfate in sulfuric acid solution.

It is often necessary to analyze iodine in sulfite solutions since such are commonly used to absorb iodine, especially after combustion technique. In such a solution it would be impossible to apply the previously mentioned catalytic methods since all involve oxidation–reduction reactions and sulfite would interfere.

In a sulfite solution whose hydrogen ion concentration is less than 2 *N*, methylene blue was found to be decolorized more or less rapidly. At an acid concentration of 2 *N*, the reduction of the dye is immeasurably slow; iodide catalyzes the

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[1] The author wishes to acknowledge with thanks the helpful criticism and suggestions of Professor J. F. McClendon, who has interested him in the field of iodine from the biochemical point of view. Abstracted from part of a thesis included among the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Minnesota.

[2] Bredig and Walton, *Z. Electrochem.*, **9**, 114 (1903).

[3] Bobtelsky and Kaplan, *Z. anorg. Chem.*, **172**, 196 (1928).

[4] Baines, *J. Soc. Chem. Ind. Trans.*, **49**, 481 (1930).

[5] Sandell and Kolthoff, THIS JOURNAL, **56**, 1426 (1934).

reaction, and the rate was found to be proportional to the iodide concentration. Free diffusion of oxygen into the solution must be prevented, although the presence of the small amount of dissolved oxygen at the beginning does no harm, as indicated by the uniformly smooth curves of color depth *versus* time (Fig. 3). Any oxygen present apparently is destroyed before the first reading of color depth can be made. The sealed narrow neck of the reaction vessel (Fig. 1) prevented the introduction of oxygen, and diffusion of the gas above into the liquid was too slow to influence the reaction rate. Bush,[6] through her studies on the reaction of sulfuric acid and potassium iodide, gave an explanation of the reaction mechanism

$$2SO_2 + 4H_2O + 2I_2 = 2H_2SO_4 + 4HI$$
$$4HI + O_2 = 2H_2O + 2I_2$$

Methylene blue may replace oxygen as oxidizing agent in the second equation. It is quite likely that the mechanism is more complicated than indicated, especially in strong acid solution, since sulfurous acid has two oxidation–reduction levels—one in which dithionous acid is formed. Although sulfurous acid does not reduce methylene blue in strongly acid solution, dithionous acid does. Furthermore, the reaction may be complicated by formation of iodine–sulfur complexes which have been shown by Foerster and Gruner[7] to have catalytic properties.

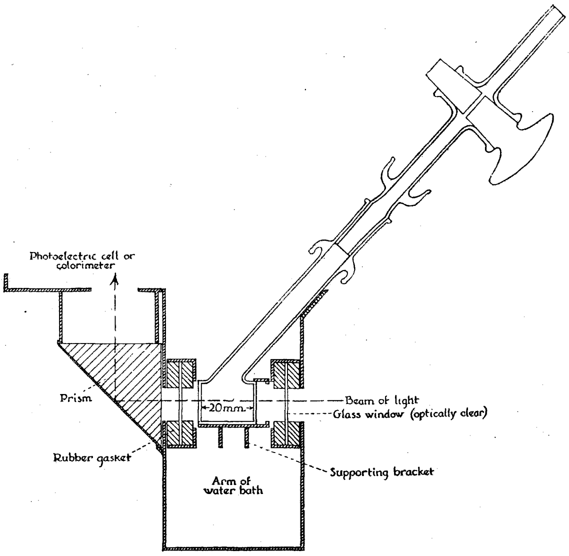

Fig. 1.

Although the mechanism is not understood, as low as 0.3 microgram of iodide may be detected, and chloride or bromide does not interfere. The closed system described below is employed to prevent free circulation of air above the liquid during the determination. Evacuation of the apparatus gave rise to erratic results when less than 5 micrograms of iodide was used. An increase in temperature increases the rate of fading of the indicator. When small quantities (0.3–5γ) of iodide are involved, the acid concentration is so great that it causes a slow decomposition of methylene blue, yielding colored products interfering with the measurement of fading time. By using the correct color filter together with the apparatus shown in Fig. 1, the color fading due to the main reaction may be successfully followed.

Apparatus.—The solution is placed in a cylindrical reaction container[8] made of optically clear glass which holds about 4 cc. of fluid. The container rests in the arm of a waterbath between two windows of optically clear glass as shown in Fig. 1. A beam of light from a constant source after passing through the fading solution is reflected upward by a prism. Its intensity can be measured either by means of a colorimeter or by a photoelectric cell.[9] The plunger of the stationary side of the colorimeter is set directly in line with the beam of light from the fading solution and the color intensity of this is compared with that of a standard solution of methylene blue in the movable cup. The amperage obtained from the photoelectric cell is directly proportional to the intensity of light falling upon it. For convenience, since it is not necessary to know the absolute value of the intensity, the reading of the microammeter may be taken as the intensity.

The light from a 400-watt lamp was monochromatized by passing through color filter H. R. Signal Red No. 243 (Corning). This filter has only 5% transmission at 608 mμ and 40% at 622 mμ; it permits the passage of the excess of red which has not been absorbed by the methylene blue and holds back the yellow color present in the fading solution.

Analytical

A. Reagents and Technique. Potassium Iodide.—Mallinckrodt Anal. Reag. (recryst.). A standard solution was prepared so that 0.1 cc. = 1 microgram of iodine (as KI).

Methylene Blue.—National Aniline Co. 88% (recryst. twice). The solution used in the reaction contained 1 g./100 cc. of water. The solution used as a standard for colorimetric comparison contained 1 mg./100 cc. of water.

Sodium Sulfite.—Merck C. P. (recryst.). A saturated aqueous solution was used.

Hydrochloric Acid.—Grasselli concentrated.

The reagents are placed in the reaction container as follows. To 0.4 cc. of a standard solution of iodide and 0.5 cc. of satd. aq. sodium sulfite are added 3.5 cc. of concentrated hydrochloric acid and 0.1 cc. of methylene blue solution (1 g./100 cc.). Calibrated Bausch and Lomb micro-

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[6] Bush, *J. Phys. Chem.*, **33**, 613 (1929).

[7] Foerster and Gruner, *Z. anorg. Chem.*, **203**, 245 (1932).

[8] Made by Bausch and Lomb Optical Company.

[9] The Duboscq type colorimeter and Weston photronic cell were used.

pipets were used for transferring the liquids. The stopcock is then closed and the reaction container is placed in a water-bath at 80°.

Measurement

A. With Colorimeter.—As the solution fades the color intensity of the standard solution of methylene blue (1 mg./100 cc.) in the movable cup is matched at intervals with the fading solution.

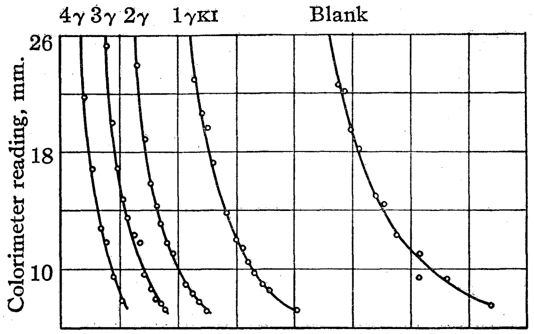

Fig. 2.

When the readings of the standard l_s are plotted against the corresponding times, t, the set of curves in Fig. 2 is obtained for the lowest range of iodine detected by the catalytic system. When the logarithm of the readings is plotted against the reciprocal of the respective times, the straight lines shown in Fig. 3 are obtained. Accordingly, the decoloration of methylene blue can be represented by the equation

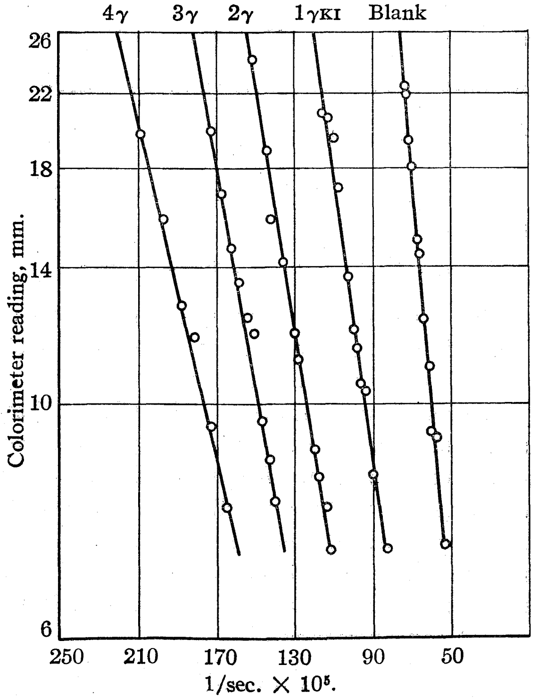

Fig. 3.

$$l/t = k \log l_s + K \qquad (1)$$

but according to Beer's law when the intensities of the two beams are equal the reading of the standard l_s is proportional to the concentration of the methylene blue in the fading solution or

$$l/t = k' \log c + K \qquad (2)$$

B. With the Photoelectric Cell.—According to Beer's law

$$C = \frac{\log I_0/I_e}{K'} \qquad (3)$$

where I_0 is the intensity of light before passing through the solution and I_e the intensity of the light which has escaped absorption at depth e and C is the concentration of the solution. On substitution of 3 in 2, the following equation is obtained

$$l/t = k' \log \frac{\log I_0/I_e}{K'} + K \qquad (4)$$

$$= k' \log \log \frac{I_0}{I_e} + K'' \qquad (5)$$

This equation expresses the relation between time and intensity of light of the fading solution as measured by the photoelectric cell. The curves obtained by plotting log log microamperage against the reciprocal of time are straight lines within limits of experimental error. Figure 4 is the curve obtained using the photoelectric cell

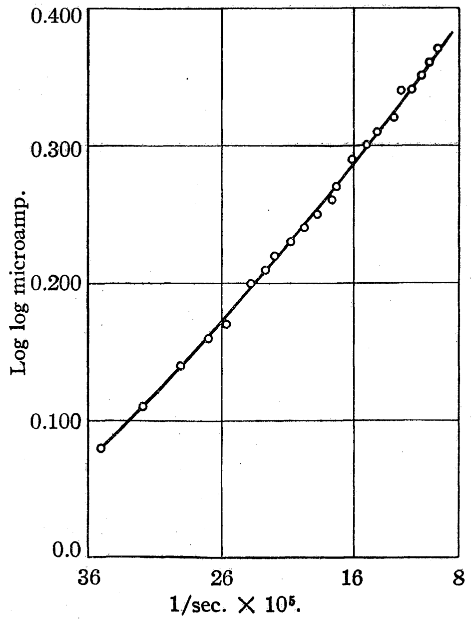

Fig. 4.

when 4 micrograms of iodine was present in the reaction solution.

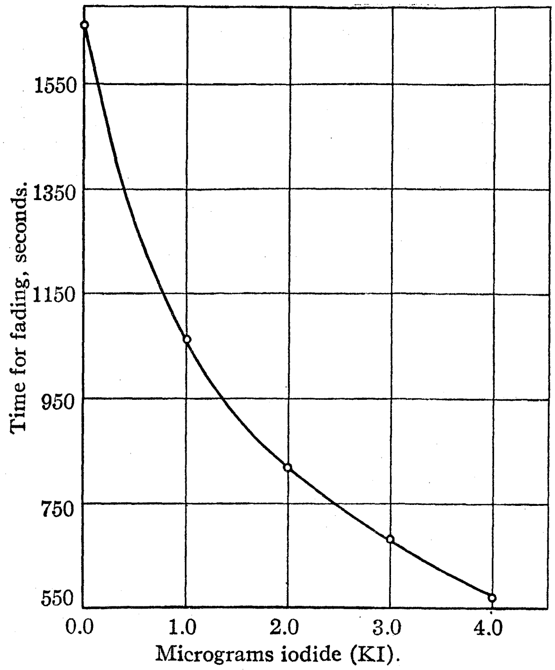

Fig. 5.

The light transmission errors, and errors due to deviation from Beer's law, for practical purposes are therefore negligible and either the colorimeter or the photoelectric cell can be used to measure the fading of methylene blue by the system.

For comparison of times for fading of methylene blue catalyzed by different concentrations of iodine a color intensity equal to 10 mm. of the standard solution of methylene blue (1 mg./100 cc.) in the movable cup of the colorimeter was chosen. When the times to reach this intensity are plotted against the corresponding concentrations of iodine, curve Fig. 5 is obtained. The method of plotting the fading curves as straight lines serves as a method of averaging the colorimetric readings.

A series of analyses carried out using this technique check within 5%.

Summary

A method for determination of iodine in sulfite solutions in concentrations up to 4 micrograms (as potassium iodide) has been devised from considerations of a system of reactions in which iodine acts as a catalyst and sulfite enters into the reaction mechanism. The method is carried out by adding hydrochloric acid and methylene blue to the sulfite solution and measuring the fading as the reaction proceeds in a specially designed apparatus.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 14, 1936

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

Electric Potentials at Crystal Surfaces, and at Silver Halide Surfaces in Particular

BY I. M. KOLTHOFF AND H. L. SANDERS[1]

With the exception of the glass electrode, very few investigators have studied the thermodynamically reversible potentials which exist at non-metallic surfaces.[2]

For various reasons a study of the potential at the interface of slightly soluble salts in equilibrium with their saturated solutions is of interest. It has been claimed by Haber[3] that this potential, π, is determined by the concentration (or, better, the activity) of the lattice ions in the solution according to the equation

$$\pi = K_c + \frac{RT}{nF} \ln a_c = K_a - \frac{RT}{nF} \ln a_a$$

in which a_c denotes the activity of the cations, and a_a that of the anions in solution. Actually Haber used ion concentrations instead of activities.

Some rough measurements[3] with silver chloride and calomel membranes were in agreement with the above equation. Recently Tendeloo[4] has made measurements with slices of minerals like heavyspar ($BaSO_4$) and fluorite (CaF_2), finding under specified conditions an approximate agreement with the foregoing equations over a limited range of concentrations.

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[1] Present address: Department of Chemistry, McGill University, Montreal, Canada.

[2] For a review of R. Beutner's work on the phase-boundary potentials between immiscible liquids see L. Michaelis, "Hydrogen Ion Concentration," Williams and Wilkins, Baltimore, Md., 1926, Chap. 8; also M. Dole, "The Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., Inc., New York, 1935, p. 380; for a review of the work of various other workers in this field see M. Cremer, "Handbuch der normalen und pathologischen Physiologie," Vol. VIII, J. Springer, Berlin, 1928, pp. 999–1053.

[3] F. Haber, *Ann. Physik,* [4] **26,** 927 (1908).

[4] H. J. C. Tendeloo, *Proc. Acad. Science, Amsterdam,* **38,** 434 (1935); *Rec. trav. chim.,* **55,** 227 (1936); *J. Biol. Chem.,* **113,** 333 (1936).

In the present paper are given the results of a more detailed study of cells involving pure silver halide membranes.

Introduction

The following cells were measured in this study

Cell I: $\mathrm{Ag/AgX(s),\ X^-(a_1)/\underset{\text{membrane}}{AgX}/X^-(a_2)/KNO_3(satd.)/}$ $\mathrm{KCl(satd.)\ Hg_2Cl_2/Hg}$

Cell II: $\mathrm{Ag/AgX(s),\ X^-(a_1)/\underset{\text{membrane}}{AgX}/X^-(a_2),\ AgX(s)/Ag}$

Cell III: $\mathrm{Ag/AgX(s),\ X^-(a_2)/KNO_3(s)/KCl(satd.),\ Hg_2Cl_2/Hg}$

in which X^- represents the chloride, bromide or iodide ion, and AgX the corresponding silver halide.

The expression for the e. m. f. of cells of types I and II can be derived by considering the reactions at each phase boundary. Suppose one faraday of electricity passes through cell I from left to right. The following reactions then take place at each phase boundary in the case of a silver chloride cell

$$\begin{aligned} \mathrm{Ag} + \mathrm{Cl^-}(a_1) &= \mathrm{AgCl(s)} + \mathrm{e} \\ \mathrm{AgCl_{memb.}} &= \mathrm{Ag^+_{memb.}} + \mathrm{Cl^-}(a_1) \\ \mathrm{Ag^+_{memb.}} + \mathrm{Cl^-}(a_2) &= \mathrm{AgCl(s)} \\ \mathrm{Hg_2Cl_2(s)} + 2\mathrm{e} &= 2\mathrm{Hg} + 2\mathrm{Cl^-(satd.\ KCl)} \end{aligned}$$

The total cell reaction is therefore the sum of these partial reactions, and is

$$\mathrm{2Ag(s) + Hg_2Cl_2(s) + 2Cl^-}(a_2) = \mathrm{2Hg + 2AgCl(s) + 2Cl^-(satd.\ KCl)}$$

The equilibrium constant of this reaction is

$$K' = (a\mathrm{Cl^-})^2_{\mathrm{satd.\ KCl}}/(a\mathrm{Cl^-})^2_2$$

Since the activity of the chloride ion in the saturated potassium chloride is constant, the equilibrium constant becomes

$$K = 1/(a\mathrm{Cl^-})^2_2$$

and the equation for the e. m. f. of cell I is then

$$\begin{aligned} E &= RT/2F \ln K + RT/2F \ln (a\mathrm{Cl^-})^2_2 \\ &= E^0 + RT/F \ln (a\mathrm{Cl^-})_2 \end{aligned}$$

It is readily shown that $E^0 = E_{\mathrm{S.C.E.}} - E^0_{\mathrm{AgCl}} = 0.246 - 0.222 = 0.024$ v.

whence $$\begin{aligned} E &= 0.024 + RT/F \ln (a\mathrm{Cl^-})_2 \\ &= 0.024 - 0.0591\ p(\mathrm{Cl^-})_2\ (25°) \end{aligned}$$

For cells of type I, then, if we neglect the small liquid junction potential between the saturated calomel reference electrode and the halide solution, the relation between the e. m. f. and $p(\mathrm{X^-})_2$ should be a straight line with slope equal to RT/F and intercept equal to the difference in e. m. f. between the saturated calomel electrode and the corresponding silver–silver halide electrode, provided there is no asymmetry potential.

It is derived from the same considerations that the e. m. f. of cells of type II should be zero at all concentrations of the halide solutions on each side of the membrane, if there is no asymmetry potential across the membrane.

Cells of type III serve to measure the actual pX value of the solutions in contact with the membrane.

The derivation of the above equation involves chloride going into solution on the left side of the membrane and deposition of chloride from the solution on the right side of the membrane in the form of silver chloride. Apparently, then, in order for cells of this type to function reversibly, one or both of the lattice ions must be able to migrate in the solid. If this condition is not fulfilled, cells of the above type cannot function.

It should be emphasized that the foregoing derivation does not involve any assumption with regard to the individual potential differences (π) at the interface on each side of the membrane, which of course are impossible to measure.

Experimental

Apparatus.—In order to overcome the high resistances in some of the systems investigated, and to eliminate possible polarizing currents from the potentiometer, an electron tube voltmeter was constructed. The design of the instrument was similar to those described by Greville and Maclagan,[5] Dubois[6] and others. An FP54 General Electric pliotron tube was used, together with a sensitive galvanometer, rated at 27,000 megohms. The method of floating grids was not employed. Tests showed that e. m. f.'s could be read to 0.1 mv. through resistances of several hundred megohms.

All measurements were made in an air-bath, held at 25.0 ± 0.1°. The bath also served to shield the silver salts from excessive exposure to light.

Materials.—Most of the work was carried on with the silver halides. For their preparation Mallinckrodt analytical grade silver nitrate proved sufficiently pure, melting without any trace of darkening—a delicate test. For preparing silver chloride, redistilled hydrochloric acid was used.

The preparation of the silver halides was carried out by slowly adding tenth molar silver nitrate solution to tenth molar halide solution in a dim red light. Conductivity water was used throughout. Occlusion of traces of silver nitrate by the silver halide results in discoloration of the latter upon fusion, but this is prevented by the use of dilute solutions. The precipitated halide was washed repeatedly by decantation.

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(5) G. D. Greville and N. F. Maclagan, *Trans. Faraday Soc.*, **27**, 210 (1931).

(6) D. Dubois, *J. Biol. Chem.*, **88**, 729 (1930).

The standard silver–silver halide electrodes used were made by silver plating platinum electrodes, then making these anodes in the appropriate tenth molar halide solution.

Silver Halide Diaphragms.—Several methods for making impermeable silver halide "electrodes" were tried. They could not be blown into bulbs like glass, nor could they be coated over glass bulbs. The Haber[3] method of melting some of the salt in the bend of a U-tube gave leaky plugs. Finally the problem was solved by melting the salt in a clean porcelain crucible in a small electric oven. The solidified melt, in disk form, about five millimeters thick, could be removed after soaking in water. These disks were then fastened over one end of a 10-mm. glass tube with sealing wax. Some 0.01 M halide solution (a_1) was poured in, and a standard silver–silver halide electrode inserted. This arrangement is termed the "crystal electrode" and is reminiscent of a MacInnes and Dole membrane glass electrode. Disk resistances were of the order of ten megohms.

In practice, our procedure was to immerse a standard silver–silver halide as well as several crystal electrodes in a solution, then measure each of these against a saturated calomel half-cell, using a saturated potassium nitrate salt bridge. The value of a_2 in cell I was varied by adding silver nitrate or sodium halide to the outer solution. In each case the value of a_2 (plotted as pX) was determined by measuring the e. m. f. between the ordinary silver halide electrode in the solution and the saturated calomel electrode, using cell III.

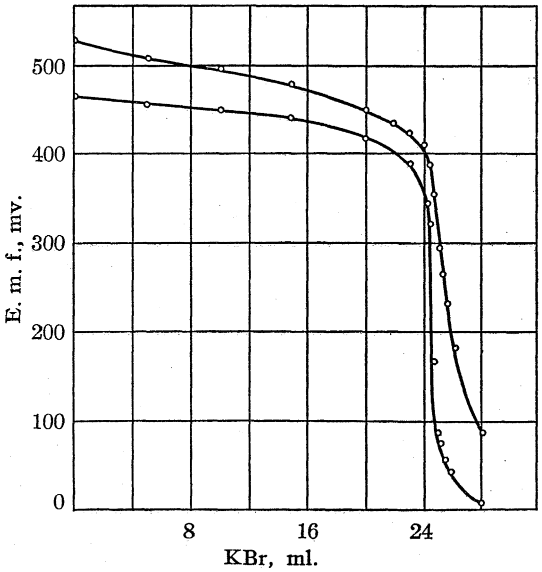

Fig. 1.—Titration of silver nitrate with bromide in the presence of potassium permanganate: upper curve, Ag–AgBr; lower curve, crystal AgBr.

Since the total e. m. f. of cell II is zero, it follows that cells I and III should have identical e. m. f. values provided that a_2 is the same in each, and there is no asymmetry potential across the membrane. Stated in other words the standard silver–silver halide electrode should give the same reading as a composite crystal electrode.

Experimental Results

Table I gives the results found on the first trial of the crystal silver chloride electrodes. The disk used had a very low asymmetry potential. Later readings were made to four decimal places.

TABLE I

COMPARISON OF SILVER CHLORIDE STANDARD AND CRYSTAL ELECTRODES

$AgNO_3$ soln. (approx.), M	E. m. f. Standard AgCl No. 6 (Cell III)	E. m. f. Crystal AgCl No. 2 (Cell I)
10^{-5}	0.279	0.280
10^{-4}	.339	.337
10^{-3}	.384	.381
10^{-2}	.453	.453
10^{-1}	.500	.500

Although, as we have pointed out, this agreement was to be expected, the objection might be raised that it was found only because a film of metallic silver had formed on the supposedly pure salt disk by accidental reduction. That this was not the case is shown by the following considerations. (1) The silver chloride disks were perfectly clear and transparent with no discoloration whatever visible. (2) On adding potassium permanganate to the solution the potential of the disk remained constant, but that of a standard silver chloride electrode changed by over 100 mv. due to an oxidation potential being set up at the metallic silver. When a disk was purposely reduced superficially with tin and hydrochloric acid, it then became sensitive to permanganate. (3) On soaking a standard and a crystal electrode in platinic chloride solution overnight, the former was spoiled, due to separation of platinum onto the silver, but the latter was unaltered. (4) A silver nitrate solution was titrated with potassium bromide in the presence of permanganate, using both standard and crystal silver bromide electrodes. As Fig. 1 shows, the former gave higher e. m. f. readings than the latter, and the break in potential at the equivalence point was less pronounced with the standard electrode, due to secondary effects.

These permanganate tests were not so conclusive in the case of crystal silver iodide electrodes, perhaps due to oxidation of the salt itself.

In Fig. 2 are shown graphically the main results of this investigation. In it the e. m. f. of cell I is plotted against the pX value of the solution. These curves are not averaged values, but are typical runs. At least six electrodes of each kind were prepared, and several runs made with each. Though the asymmetry potentials changed several millivolts between runs, all satisfactory electrodes showed a constant linear relation on consecutive runs. About four out of five of the crystal electrodes prepared were considered satisfactory.

Equilibrium potentials were established very quickly whether or not the solution around the electrode was pre-saturated with the appropriate silver halide; in most of the runs it was saturated, however.

The silver chloride line had a slope of 0.0579, the silver bromide of 0.0574—both slightly less than the theoretical value of 0.0591 at 25°. With silver iodide, the precision was not as great as with the other two electrodes, as seen by Fig. 2. In this case the slope of the line was 0.052.

If these lines are extrapolated to $pX = 0$, the following values for the cell E^0 are found: E^0(AgCl) = +0.020 v.; E^0(AgBr) = +0.160 v.; E^0(AgI) = +0.380 v. Taking the potential of the saturated calomel electrode as 0.246 v., the following are the calculated values: E^0(AgCl) = +0.024 v.; E^0(AgBr) = +0.175 v.; E^0(AgI) = +0.398 v.

The agreement between the experimental and calculated values is very good in the case of silver chloride membranes, indicating that the asymmetry potential is very small (4 mv.); in the case of silver bromide, the asymmetry potential was usually found to be of the order of 15 mv., and with silver iodide of 18 mv. The asymmetry potentials depend upon the method of preparation and the age of the membranes, their magnitude decreasing with age.

Certain writers seem to have thought that pure silver halide electrodes may be obtained by coating a platinum wire with the salt. Thus Hiltner[7] melted silver chloride round a platinum wire using a blast lamp flame, and found satisfactory behavior. We carefully melted silver bromide about a silver wire in the electric oven. The cooled mass was clear, the imbedded length of the wire being plainly visible through the transparent salt. Such a "rod" type of electrode showed a fluctuating and indefinite potential, which changed greatly on mere agitation of the solution. Similar results were found with silver chloride. Since the silver halides are not electronic conductors they naturally cannot behave as metallic electrodes because no reversible electron reaction can occur at their surface.

Finally, the effects of various ions on the crystal electrode potentials were studied. In a solution saturated with potassium nitrate the silver bromide membrane electrode cells again gave linear e. m. f.–pX curves at all concentrations of bromide ion used, the slopes being about the same as those found in the absence of the nitrate. The silver chloride membrane cells showed no changes in potential upon addition of small amounts of hydrogen, lead or thallous ions. Ions which are supposedly potential-determining, like chloride and bromide, failed to affect the potentials of the silver iodide membranes under conditions at which no chemical precipitation could occur.

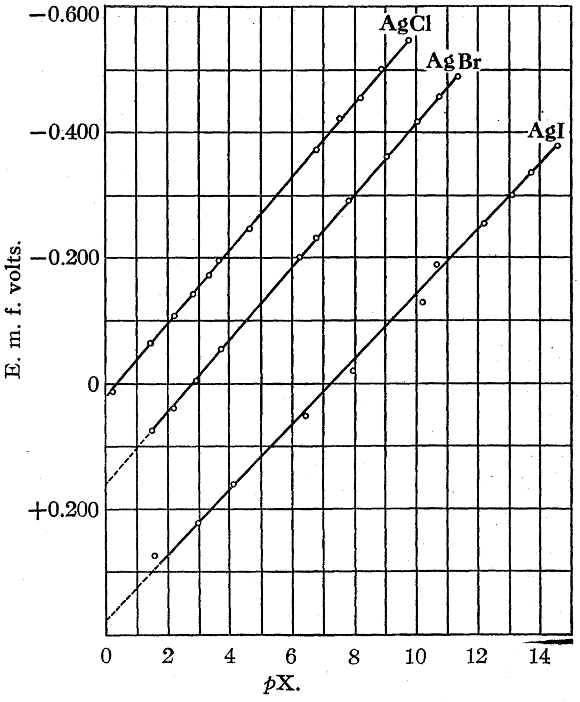

Fig. 2.—Change of potential of silver halide surfaces.

Following much the same technique as above, an attempt was made to duplicate the results of Haber with paraffined calomel tablets, and of Tendeloo with heavyspar and fluorite, but with no success, the observed potentials being unreproducible, and changing upon the addition of any ion. Our results with the fluorite electrode are in agreement with those reported recently by Anderson[8] who, contrary to Tendeloo, found that the calcium fluoride membrane did not function as a calcium electrode.

It is hoped to extend this work and discuss some of its theoretical implications in the near future.

Acknowledgment.—The junior author wishes

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(7) W. Hiltner, "Ausführung potentiometrischer Analysen," Verlag Julius Springer, Berlin, 1935.

(8) R. S. Anderson, *J. Biol. Chem.*, **115**, 323 (1936).

to express his gratitude to McGill University, Montreal, for its award of the Moyse Travelling Scholarship, which enabled him to do this work. We are particularly indebted to Professor F. H. MacDougall for his aid in the derivation of the equations presented in the first part of this paper.

Summary

An expression has been derived for the e. m. f. E of cells involving silver halide membranes, of the type

$$\mathrm{Ag/AgX(s),\ X^-(}a_1\mathrm{)/\underset{membrane}{AgX}/X^-(}a_2\mathrm{)/KNO_3(sat.)//KCl(sat.),\ Hg_2Cl_2/Hg}$$

It was found that

$$E = E^0 + RT/F \ln (a_2)$$

The experimental results obtained with fused silver halide membranes over a wide range of values of a_2 showed that $E = E^0 + A \ln(a_2)$ in which A was found to be slightly less than the theoretical value.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 3, 1936

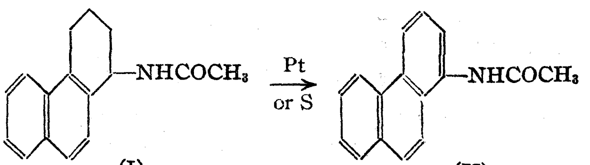
NOTES

A New Synthesis of 1-Aminophenanthrene

BY W. E. BACHMANN

Recently[1] we described the preparation of 1-aminophenanthrene, starting from phenanthrene. This new phenanthrylamine can also be obtained from naphthalene through the intermediate compound, 1-keto-1,2,3,4-tetrahydrophenanthrene. The oxime of this cyclic ketone is reduced by sodium amalgam and alcohol to 1-amino-1,2,3,4-tetrahydrophenanthrene[2] and the acetyl derivative (I) of the amine is dehydrogenated to 1-acetylaminophenanthrene (II). The free base, 1-aminophenanthrene, can be obtained by hydrolysis of the acetyl derivative.

Complete dehydrogenation of 1-acetylamino-1,2,3,4-tetrahydrophenanthrene takes place rapidly when the compound is heated with half its weight of platinum black at 320°; the 1-acetylaminophenanthrene is obtained pure by a single recrystallization from benzene. We have also employed sulfur for the dehydrogenation; with this reagent some oily by-products are formed in the reaction, but the 1-acetylaminophenanthrene can be isolated in pure form in yields of 50–60%.



(I) (II)

Experimental

1 - Acetylamino - 1,2,3,4 - tetrahydrophenanthrene.—A mixture of 13 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene,[3] 6 g. of hydroxylamine hydrochloride and 8 cc. of pyridine in 80 cc. of absolute alcohol was heated on a steam-bath for three hours. The solution was evaporated to dryness and the residue was digested with water. The oxime, which was formed in quantitative yield, was filtered off and when dried was sufficiently pure for the next step.

A mixture of 13 g. of the oxime and 180 cc. of alcohol was warmed to 50–60° and treated with 150 g. of 2% sodium amalgam in portions in the course of half an hour. Throughout the reaction the temperature was kept below 60° by external cooling and the solution was kept acidic by addition of acetic acid. Any sodium acetate that precipitated was brought back into solution by addition of small amounts of water. When the reaction was complete, the solution was separated from the mercury and the alcohol was evaporated. The residue was taken up in water and a small amount of oily impurities was removed by extraction with carbon tetrachloride. The aqueous solution was made alkaline and the 1-amino-1,2,3,4-tetrahydrophenanthrene was extracted by benzene. Evaporation of the benzene left the amine as an oil which quickly solidified. A mixture of the crude amine and 15 cc. of acetic anhydride was refluxed for five minutes. The acetic acid and the excess of acetic anhydride were removed by directing a jet of air onto the warm solution. The crystalline residue of the acetyl derivative was digested with cold acetone and the colorless crystals were filtered off; yield, 10 g. 1-Acetylamino-1,2,3,4-tetrahydrophenanthrene crystallizes from acetone in colorless needles; m. p. 176°. The compound is not very soluble in cold acetone but dissolves in benzene and in acetic acid.

Anal. Calcd. for $C_{16}H_{17}ON$: N, 5.9. Found: N, 6.0.

Dehydrogenation of 1-Acetylamino-1,2,3,4-tetrahydrophenanthrene.—A mixture of 10 g. of 1-acetylamino 1,2,3,4-tetrahydrophenanthrene and 2.5 g. of sulfur was

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[1] Bachmann and Boatner, THIS JOURNAL, 58, 2097 (1936).

[2] Our experiments on the preparation of this compound were already completed at the time Burger and Mosettig [*ibid.*, 58, 1570 (1936)] reported its preparation by the same method.

[3] Haworth, *J. Chem. Soc.*, 1128 (1932).

heated at 250–260° in a distilling flask having a wide side-arm sealed to a receiver. After half an hour, when evolution of hydrogen sulfide had ceased, the product was distilled at 0.5 mm. pressure. Recrystallization of the distillate from benzene yielded 5 g. of 1-acetylaminophenanthrene in the form of colorless needles; m. p. 219–220°. From the benzene filtrate there was obtained 1.5 g. of unchanged tetrahydro derivative which can be used in another dehydrogenation reaction. The 1-acetylaminophenanthrene was identical with the product obtained by acetylation of 1-aminophenanthrene prepared through the Beckmann rearrangement.[1] On hydrolysis by twenty-four hour boiling with an alcoholic solution of hydrochloric acid the acetyl derivative was converted completely to 1-aminophenanthrene; m. p. 146–147°.

CHEMISTRY LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
RECEIVED DECEMBER 14, 1936

The Action of Benzylamine on Aliphatic Esters

BY C. A. BUEHLER AND CHARLES A. MACKENZIE

In an attempt to develop an improved method for the identification of aliphatic esters, they were treated with benzylamine in aqueous solution. This scheme is similar to that already in use for certain halogenated aliphatic esters which, with ammonium hydroxide in the cold, form the corresponding amides. Both these reagents possess approximately the same dissociation constants, but it appeared that benzylamine, in contrast to ammonia, might be employed successfully at boiling temperatures with the esters of weaker acids because of its higher boiling point.

From Tables I and II it can be seen that benzylamine reacts with the esters studied either to form the N-benzylamide or the benzylamine hydrohalide. With the polyhalogenated esters investigated, the corresponding N-benzylamides form readily even in the cold. Of the monohalogenated esters studied, only one, ethyl chloroacetate, could be induced to undergo a similar reaction. This type, by the more vigorous treatment used for non-halogenated esters or, preferably, by heating with the amine in the absence of water, yields the benzylamine hydrohalide, a reaction[1] which has been represented as

$$XCH_2COOR + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2NHCH_2COOR + C_6H_5CH_2NH_2 \cdot HX$$

By refluxing from one to five hours, depending upon the strength of the acid present in the ester, the non-halogenated esters produced N-benzylamides. All the esters, save those of the higher fatty acids, gave satisfactory yields.

TABLE I

N-BENZYLAMIDES FROM ESTERS OF NON-HALOGENATED ACIDS

Ester	Formula	M. p., °C. Obsd.	Corr.	Lit.	Nitrogen, % Calcd.	Found
Ethyl formate	$HCONHCH_2C_6H_5$	59.6–60.2	59.8–60.4	49[a]	10.37	10.46
Methyl acetate[b]	$CH_3CONHCH_2C_6H_5$	60.4–61.0	60.7–61.3	60–61[c]		
Ethyl propionate	$C_2H_5CONHCH_2C_6H_5$	42.6–43.7	42.6–43.7		8.58	8.46
Ethyl *n*-butyrate	$C_3H_7CONHCH_2C_6H_5$	36.9–38.0	36.9–38.0		7.91	7.89
Ethyl *i*-butyrate	$C_3H_7CONHCH_2C_6H_5$	86.3–87.3	87.0–88.0		7.91	8.07
Ethyl *n*-valerate	$C_4H_9CONHCH_2C_6H_5$	41.1–41.8	41.1–41.8		7.33	7.38
Ethyl *n*-caproate	$C_5H_{11}CONHCH_2C_6H_5$	50.1–51.2	50.3–51.4		6.83	6.88
Ethyl crotonate	$C_3H_5CONHCH_2C_6H_5$	111.1–112.2	112.5–113.6		8.00	7.96

[a] Holleman, *Rec. trav. chim.*, **13**, 415 (1894). [b] Identical results were obtained with ethyl, propyl, butyl, isobutyl, *s*-butyl, amyl and isoamyl acetates. [c] Amsel and Hofmann, *Ber.*, **19**, 1286 (1886).

TABLE II

COMPOUNDS FROM ESTERS OF HALOGENATED ACIDS

Ester	Formula	M. p., °C. Obsd.	Corr.	Lit.	Nitrogen, % Calcd.	Found
Ethyl chloroacetate	$ClCH_2CONHCH_2C_6H_5$[a]	92.2– 92.8	93.0– 93.6	93.5– 94.5 (corr.)[b]		
Ethyl chloroacetate	$C_6H_5CH_2NH_2 \cdot HCl$[c]	257.0–259.0	263.6–265.7	255.5–258.0[d]	9.75	9.79
Ethyl bromoacetate	$C_6H_5CH_2NH_2 \cdot HBr$[e]	218.0–219.0	223.0–224.1	215–216[f]	7.45	7.52
Ethyl dichloroacetate	$Cl_2CHCONHCH_2C_6H_5$	94.2– 95.0	94.8– 95.6	95–96[g]		
Ethyl trichloroacetate	$Cl_3CCONHCH_2C_6H_5$	92.8– 93.6	93.6– 94.4	90–91[h]	5.55	5.59

[a] Prepared by method described for polyhalogenated esters. [b] Jacobs and Heidelberger, *J. Biol. Chem.*, **20**, 686 (1915). [c] Ethyl α-chloropropionate gave the same product. [d] Hoogewerff and van Dorp, *Rec. trav. chim.*, **5**, 253 (1886). [e] Ethyl β-bromopropionate and ethyl α-bromo-*n*-butyrate gave the same product. [f] Wallach, *Ann.*, **259**, 308 (1890). [g] Mannich and Kuphal, *Arch. Pharm.*, **250**, 544 (1912). [h] Braun, *Ann.*, **453**, 143 (1927).

Experimental

Preparation of Ester Derivatives

(a) **Polyhalogenated Esters.**—A mixture of 0.5 cc. of ester, 2 cc. of benzylamine and 0.5 cc. of water was im-

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[1] Mason and Winder, *J. Chem. Soc.*, **65**, 187 (1894).

mersed in an ice-bath and shaken vigorously at intervals of a few minutes until a solid formed. Purification of the solid was effected by recrystallization from ligroin.

(b) **Monohalogenated Esters.**—Although the derivatives of monohalogenated esters may be prepared as in (c), a better procedure is to heat 2 mols of the amine with 1 mol of the ester for a few minutes when the hydrohalide forms. To obtain the salt in pure form, it was dissolved in hot ethyl acetate containing sufficient ethyl alcohol to effect solution, after which the solid crystallized from the cooled solution upon the addition of a few cc. of ether.

(c) **Non-halogenated Esters.**—The ester, 2 cc., mixed with 4 cc. each of benzylamine and water and, when necessary, sufficient ethyl alcohol or dioxane to effect solution, was refluxed one hour (for formates), two hours (for acetates) or from four to five hours (for higher esters like caproates). The excess of reagents was removed by distilling up to 200°, after which the derivative[2] in the distillation flask was crystallized from hot ligroin by cooling to room temperature or lower.

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(2) Before final crystallization, derivatives melting below 50° were distilled off over a range beginning at 290° and continuing until decomposition occurred in the distillation flask.

DABNEY CHEMICAL LABORATORY
UNIVERSITY OF TENNESSEE
KNOXVILLE, TENN.
RECEIVED OCTOBER 28, 1936

The Thermal Decomposition of Gaseous Hydrogen Peroxide

BY G. B. KISTIAKOWSKY AND S. L. ROSENBERG[1]

The thermal decomposition of gaseous hydrogen peroxide was investigated semi-quantitatively by a static method at 85 and 98°. A very pure, 70% peroxide was used. The reaction in a quartz flask is heterogeneous, with an almost negligible temperature coefficient. Times for 50% reaction varying from one to thirty minutes were obtained, the reaction rate increasing with time due to changes in the reaction vessel surface. No stopping of the reaction at about 15% completion as described by Elder and Rideal[2] could be detected. Furthermore, the pressure increase accompanying the reaction proved to be the theoretical value of 50% (based on hydrogen peroxide present), rather than the somewhat astonishing value of about 1000% found by these authors.

Some experiments were tried, where the reaction vessel was flushed with oxygen prior to the reaction. This had no effect, so that neither oxygen from the reaction nor other oxygen leads to a stoppage of the reaction before completion. In another experiment a thin coating of paraffin wax was applied to the interior of the quartz reaction bulb. This slowed down the reaction somewhat, demonstrating its heterogeneity.

We take this opportunity of thanking Mr. P. Giguere of McGill University for the gift of some very pure 70% hydrogen peroxide.

HARVARD UNIVERSITY
CAMBRIDGE, MASS.
RECEIVED DECEMBER 18, 1936

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(1) McGill University Moyse traveling fellow.

(2) Elder and Rideal, *Trans. Faraday Soc.*, **23**, 545 (1927).

Syntheses from Ethanolamine. IV. A Synthesis of β-Chloroethyl Phthalimide

BY HENRY WENKER

This paper presents a convenient method of preparing β-chloroethyl phthalimide, an intermediate which can be used for most purposes in place of the less readily accessible β-bromo analog.[1] The reactions involved are: phthalic anhydride and ethanolamine react in molar proportions to form β-hydroxyethylphthalimide; this compound reacts with one mole of phosphorus pentachloride to yield β-chloroethyl phthalimide.

Experimental

Garelli and Racciu[2] obtained β-hydroxyethyl phthalimide from phthalic anhydride and ethanolamine, using absolute ethanol as a solvent. It has been found that by omitting the solvent and heating both components[3] for about thirty minutes to 210°, a quantitative yield is obtained. On cooling, the product solidifies in crystalline form, melting at 127–128° (lit. 127–128°). Through the action of phosphorus pentachloride, β-chloroethyl phthalimide was obtained from this product in the usual way. The yield was 94%, the melting point 81° (lit. 79–81°).

ELIZABETH, N. J.
RECEIVED DECEMBER 4, 1936

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(1) "Organic Syntheses," John Wiley and Sons, Inc., 1932, Coll. Vol. I, p. 114.

(2) Garelli and Racciu, *Atti acad. sci. Torino, Classe sci. fis, mat. nat.*, **69**, I, 358–63 (1934).

(3) Technical monoethanolamine, boiling at 169–171°, from Carbide and Carbon Chemicals Corporation, was used.

COMMUNICATIONS TO THE EDITOR

BENZANTHRONE AND 4-PHENYLBENZANTHRONE

Sir:

In a recent elaboration of their former work, Charrier and Ghigi [*Ber.*, **69**, 2211 (1936)] have suggested that in our study of Grignard addition to benzanthrone [This Journal, **57**, 740 (1935)] we failed to concede priority to them. We regret that our mode of presentation failed to make clear that the Italian workers first proved two instances of 1,4-addition of the Grignard reagent to benzanthrone and predicted the structure of 4-phenylbenzanthrone.

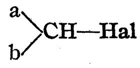
McGill University C. F. H. Allen
Montreal, Canada S. C. Overbaugh

Received January 8, 1937

WALDEN INVERSION IN SUBSTITUTION REACTIONS ON INORGANIC COMPLEX COMPOUNDS

Sir:

Recently Bailar, Haslam and Jones [This Journal, **58**, 2226 (1936)] have published an interesting paper on the steric course of the substitution reaction between *l*-dichloro-diethylene-diamino-cobaltichloride and 2 moles of ammonia which leads to a *levo*-product at low, to a *dextro*-product at high, temperature. Since the theoretical considerations about Walden inversion on which the paper is based are likely to be misunderstood, I would like to draw attention to the following point. According to the authors, Bergmann, Polanyi and Szabo [*Z. physik. Chem.*, **20B**, 161 (1933); *Trans. Faraday Soc.*, **32**, 843 (1936)] in their theory of Walden inversion predict that each reaction involving a single step in substitution on the tetrahedral carbon atom will bring about inversion, an even number of substitutions therefore reproducing the original configuration. In the above case, this apparently is not always the fact. As a matter of fact, Bergmann, Polanyi and Szabo are concerned expressly with substitutions of polar bonds by ions;[1] they assert that substitution of such a polar bond by a negative ion is necessarily connected with configurational inversion, while substitution by a positive ion leads either to the initial configuration or to a racemic product. The reaction under discussion does not involve a substitution by ions, and especially not by negative ions; it reminds one of the well-known observation of Senter and co-workers [*J. Chem. Soc.*, **107**, 638 (1915); **109**, 1091 (1916); **117**, 140, 151 (1918)] that *l*-phenylchloroacetic acid by interaction with ammonia in water or alcohol gives *d*-, in acetonitrile or liquid ammonia *l*-phenylaminoacetic acid, or the experiments of Holmberg [*Ber.*, **60**, 2194, 2198 (1927)] on the relationship between the rotation of xanthogeno-succinic acid and the temperature at which it was prepared from active bromosuccinic acid. The theory of Bergmann, Polanyi and Szabo does not make any prediction for such cases.

It may be added that in the group of these octahedral complexes some substitutions by negative ions are already known to be accompanied by configurational inversion. Without discussing the whole existing material, reference may be made to the following two reactions: (*a*) *cis*-Chloro-isorhodanato-diethylenediamino-cobaltic ion is converted by means of rhodanide ions into *trans*-diisorhodanato-diethylenediamino-cobaltic ion [A. Werner, *Ann.*, **386**, 1 (1912)]. (*b*) *trans*-Chloro-isorhodanato-diethylenediamino-cobaltic salts are converted by hydroxide ions (aqueous ammonia solution) into *cis*-hydroxoisorhodanato-diethylenediamino-cobaltic salts. Likewise, the auto-racemization observed in some of the inorganic complex compounds may be due to the same mechanism as the racemization of  $\overset{a}{\underset{b}{>}}\mathrm{CH{-}Hal}$ by halogenide ions, *e. g.*, the autoracemization of dichloro-diethylenediamino-cobaltic chloride to the substitution of the inner chloro atoms by negative chloride ions. [Werner, *Ber.*, **44**, 3279 (1911); **45**, 3294 (1912), suggested that the racemization is caused by aquation, but this has never been proved by isolation of a chloroaquo-diethylene-diamino-cobaltic salt.] Of course, we cannot predict whether all the known cases fit into our simple scheme, but we hope to come to some definite conclusions in the course of our further investigations on Walden inversion.

The Daniel Sieff Research Institute
Rehovoth, Palestine Ernst Bergmann

Received December 30, 1936

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[1] It may be added that the afore-mentioned inorganic complex salt has an octahedral, not a tetrahedral, structure, but the theory should really be extendable to this case.

THE EFFECTS OF SULFURIC ACID AND OF ZINC CHLORIDE ON THE MAIN RAMAN BAND OF WATER

Sir:

In the course of a systematic study of the effects of dissolved salts, acids, and bases on the Raman spectrum of water, we have found that sulfuric acid and zinc chloride produce unique changes in the shape and in the frequency of the maximum of the main band, which are illustrated in the accompanying figures. The shift in the maximum is related to the concentration as follows, at 40°.

H_2SO_4, % by wt.	$\Delta\Delta\nu$, cm.$^{-1}$	$ZnCl_2$, % by wt.	$\Delta\Delta\nu$, cm.$^{-1}$
0.0	0	0.0	0
15.3	+ 14	14.3	+ 9
25.6	+ 34	31.6	+58
65.0	+ 32	41.8	+78
80.0	+ 20	50.0	+91
95.0	−336	57.1	+82

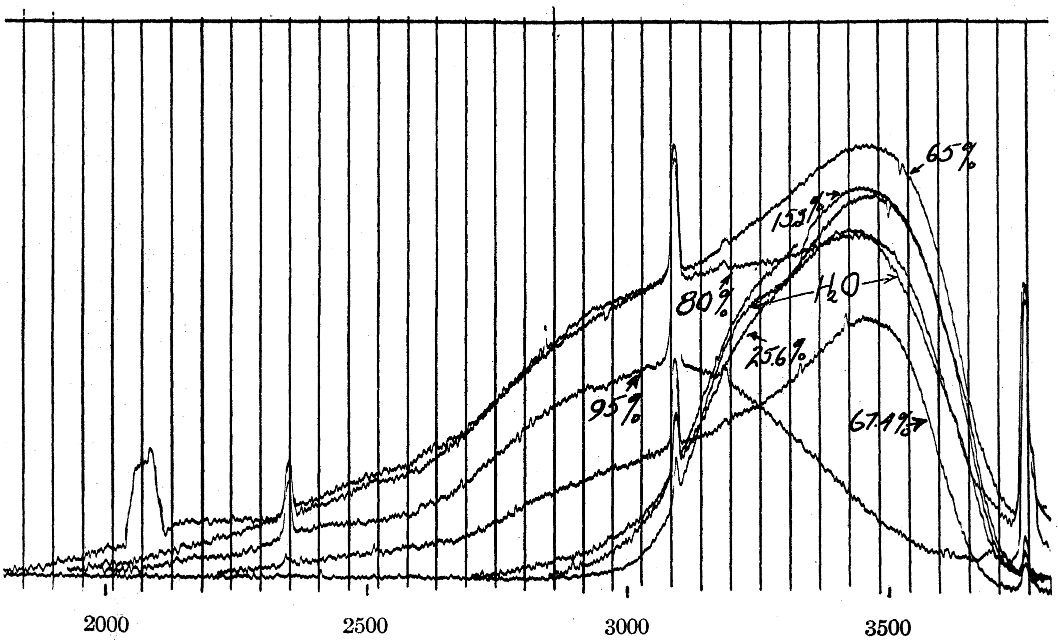

Fig. 1.—Showing the effect of various concentrations of sulfuric acid on the main Raman band of water.

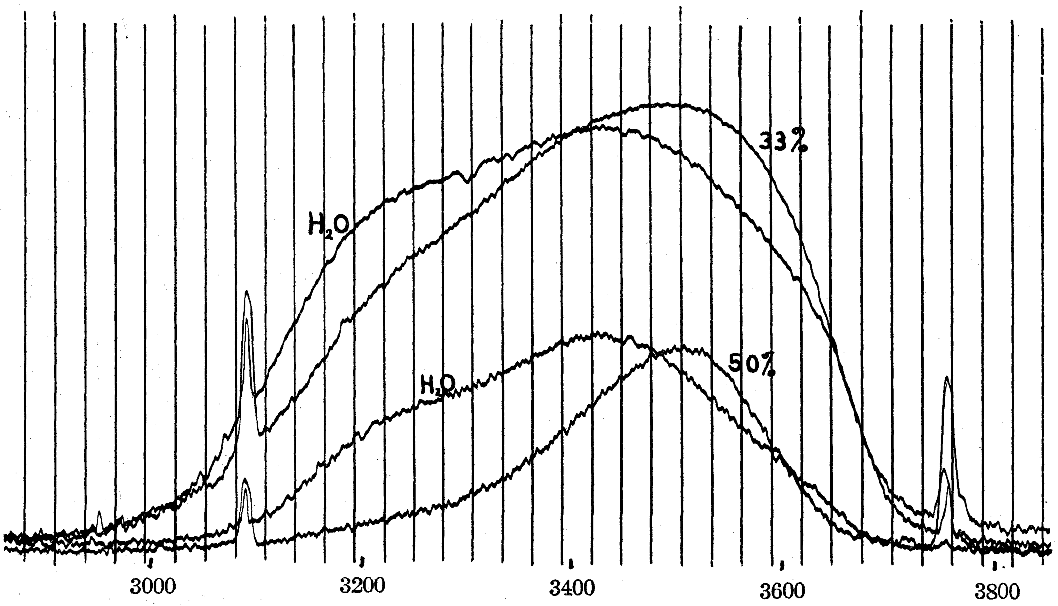

Fig. 2.—Showing the effect of 33% and 50% zinc chloride on the main Raman band of water.

The apparent broadening of the water band toward lower frequencies in sulfuric acid solutions of medium concentration (Fig. 1) is shown by the spectrum of 95% sulfuric acid to be due to the appearance of a new band, almost symmetrical in shape and with maximum at 3094 cm.$^{-1}$. A band at this frequency in pure sulfuric acid can only arise from a hydrogen or O–H vibration. Its width shows definitely that sulfuric acid is associated in the same manner as water and its change in intensity with dilution should be a function of the degree of ionization of sulfuric acid. In spite of the broadening toward lower frequencies, at concentrations below 65% the shift of the maximum toward higher frequencies in sulfuric acid is much larger than that in corresponding concentrations of sodium sulfate.

Like the alkaline earth chlorides, addition of zinc chloride to water causes the short frequency [ν(H)] component of the main band to disappear, indicating a dis-association of the solvent. While the net effect of this disappearance with the former compounds is to make the whole band more symmetrical, zinc chloride increases the asymmetry of the band and produces some three times as great a shift of the maximum as do alkaline earth chlorides in corresponding concentrations. The shift, which probably arises from and is an indication of the strong hydration of the zinc ion, increases up to a concentration corresponding approximately to one Zn^{++} to seven molecules of H_2O, it decreases with increasing concentration beyond that point.

STANFORD UNIVERSITY
CALIFORNIA
PHILIP A. LEIGHTON
JOHN BURNHAM

RECEIVED DECEMBER 28, 1936

INHIBITORY EFFECT OF PACKING ON THE METHYL ETHER DECOMPOSITION

Sir:

In their work on the kinetics of methyl ether decomposition, Hinshelwood and Askey [*Proc. Roy. Soc.* (London), **A115**, 215 (1927)] found that the rate in a silica bulb half-filled with powdered silica was appreciably lower than in a completely empty bulb. Thus at about 535° and 175 mm. initial pressure the values of t_{50} were 6.2 and 5.4 minutes for half-filled and empty bulbs, respectively. The packing thus decreased the rate by about 14%.

This effect, if real, is in harmony with the conclusion of Rice and Herzfeld [THIS JOURNAL, **56**, 284 (1934)] that the methyl ether decomposition involves long chains, the inference being that the chains may be broken at a silica surface by catalytic re-combination of the carriers. In order to obtain confirmation of the result, the following experiment was carried out.

Two Pyrex tubes, one empty and the other filled with 5 mm. Pyrex chips coated with potassium chloride, were bound together in a copper jacket and placed in an electric heater. Methyl ether vapor was introduced simultaneously into the two bulbs, and pressure differences and total pressures were determined.

The rate of pressure increase was definitely lower in the packed tube. In an experiment at 481°, the initial pressures were 458 and 440 mm. in packed and empty tubes, respectively. After twenty minutes, the corresponding pressures were 617 and 610 mm., giving increases of 159 and 170 mm. Correcting the latter for the lower initial pressure and for a small expansion (0.5%) gives 180 mm. for the corresponding pressure increase. The packing thus decreased the rate of pressure increase by 11.5%, as compared with the 14% reported by Hinshelwood and Askey.

It would seem to be clear that the reaction is not the simple homogeneous process originally postulated by Hinshelwood and Askey.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
ROBERT N. PEASE

RECEIVED JANUARY 6, 1937

NEW BOOKS

Elementary Principles in Physical Chemistry. By T. J. Webb, Assistant Professor of Physical Chemistry, Princeton University. D. Appleton–Century Company, Inc., 35 West 32d Street, New York, N. Y., 1936. 344 pp. 15.5 × 23 cm. Price, $4.00.

As an introductory text in physical chemistry, this book is somewhat unconventional in choice of subject matter. This is doubtless in part due to the fact that it is written, according to the sub-title, "with special reference to the state of equilibrium in a chemical reaction and to the rate of attainment of equilibrium." As a result electrical conductance, for example, is treated with brevity and the phenomena of transference are largely omitted; similarly absent are the usual chapters on the liquid state, the solid state, the relation of physical properties to molecular constitution, and the colloidal state. Since rates of reaction are a primary object, the absence of a discussion of photochemical reactions is more difficult to understand. Subjects which are treated somewhat more fully than is usual in introductory texts are distribution laws (both Maxwell's and quantum theory), thermodynamics (making free use of entropy), the Debye–Hückel theory of electrolytes and its application to reaction rates, Eyring's theory of reaction rates, and Schrödinger's equation.

Numerous interesting tables of numerical results are included, but experimental methods receive scant attention. Consequently a student with no more than the usual experience of one beginning physical chemistry would often find himself studying theories of phenomena in advance of any appreciation of the facts; the extent to which this would create difficulty would depend upon the instructor. Since the treatment is largely analytical rather than descriptive, a student without a fair knowledge of calculus would lose much that is most useful in the book.

While it is possible to disagree with various details, on the whole the book gives evidence of having been thoughtfully written. The student who is interested primarily in the practical application of physical chemistry may perhaps not be attracted; but the student whose taste is for theoretical aspects of the subject, including those of fairly recent origin, will find much to interest him.

Roscoe G. Dickinson

Quantitative Analyse. (Quantitative Analysis.) By Dr. Otto Brunck, Professor em. an der Bergakademie Freiberg. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1936. 224 pp. 8 figs. Price, RM. 9.

"The Art of Gravimetric Analysis at Freiberg" would be a more exact title for this book. Professor Brunck presents the procedures of classical gravimetric analysis developed there by Clemens Winkler and enriched by his own life work. One sees on every page that the methods described have, as the author states in the preface, been tested with his own hands.

The first sixty-seven pages of the book are devoted to the general technique of quantitative analysis. Since Professor Brunck omits all chemical theory with which the student is presumably acquainted from previous study of qualitative analysis, a very thorough and helpful treatment of the practical operations such as fusions, filtrations, and ignitions is possible. A section on electroanalysis is included.

The remaining one hundred forty-seven pages are given to particular directions for the determination of water, the metals, and the non-metals. Besides the common metals of qualitative analysis, gold, platinum, palladium, molybdenum, tungsten, titanium, uranium, and beryllium are treated. At the end of each group of metals, directions for separation are added. In this part of the book repetition is avoided and cross reference is made easy by a very clear system of paragraph numbering.

It is easy to find flaws in a book written in the spirit of this one. Not all analysts will agree that calcium may be separated from magnesium by a single precipitation in alkaline solution and that the practice of weighing calcium as the oxide is to be abandoned. Many useful methods, such as the separation of iron, titanium, and other elements with cupferron, and the determination of sodium with uranyl acetate reagents, are not even mentioned. One regrets that Professor Brunck has limited the scope of his book through economic considerations. The lack of references is particularly unfortunate. Perhaps the most serious objection to the book as a text is that in many cases it would lead a student to employ gravimetric methods where volumetric methods are more suitable.

For these reasons the book is not to be recommended as a text for elementary quantitative analysis. It will be valuable, however, to more experienced workers, and teachers of quantitative analysis will find it most suggestive and stimulating.

Charles H. Greene

Die neuere Harnsäurechemie. Tatsachen und Erklärungen. (Modern Theories and Researches on the Chemistry of the Uric Acids.) By Prof. Dr. Heinrich Biltz, Breslau. Verlag Johann Ambrosius Barth, Salomonstrasse 18B, Leipzig C 1, Germany. 164 pp. 14.5 × 22.5 cm. Price, RM. 5.80.

Professor Biltz's investigations on glyoxalones led him to make a searching study of the complicated chemistry of uric acid. As a result, his newer investigations have contributed much important and valuable data leading to a better understanding of the chemistry and reactivity of uric acid, especially the nature of the 4,5 double bond in this oxypurine molecule. The conclusions and theoretical discussions of the author are reported under five subdivisions or chapters which may be expressed as follows: (1) purine constructions of the uric acid type in which the 4,5 double bond of the uric acid molecule is resistant to change; (2) derivatives of uric acid resulting from a rupture of the pyrimidine ring in the uric acid molecule; (3) derivatives of uric acid formed by rupture of the glyoxalone ring of this purine molecule; (4) chlorination products formed from uric acid and their characteristic reaction products and (5) characteristic caffolide and spirohydantoin ring compounds formed from uric acid. The author makes original applications of the electron conception of chemical action to explain many of the results obtained by experimentation, and uses this method of reasoning to explain the disagreement in chemical behavior between uric acid and xanthine. The author considers the 4,5 double bond in the uric acid molecule as a normal ethylene grouping, while in xanthine it functions in an entirely different manner as a result of its conjugation with a double bond in the 7,8 or 8,9 positions of the purine molecule.

Under these five subdivisions are discussed (1) uric acid and xanthine reactions, uric acid acidity, alkylation and acylation, hydrolytic degradation and oxidation, (2) uric acid glycols and their characteristic degradation changes, oxidation reactions with conversion to hydantoins and formation of allantoin, (3) the acetal derivatives of uric acid glycol, their behavior toward acids, reduction with hydriodic acid and interaction with diazomethane, (4) isouric acid derivatives, halogenated dihydrouric acids and pseudouric acids, and (5) the caffolides and formation of hydantoylamides, spirohydantoins and their conversion into hydantoins.

The books contain a large amount of most interesting data accumulated after years of research on uric acid. Abundant literature references are given which will be very helpful to the inexperienced worker in this field of chemistry. What is greatly needed, however, is a better organized system of classification of characteristic reactions to make the book more readable.

Treat B. Johnson

Physical Chemistry. By Frank H. MacDougall, M.A., Ph.D., Professor of Physical Chemistry, University of Minnesota. The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1936. ix + 721 pp. 97 figs. 14.5 × 22.5 cm. Price, $4.00.

Another text-book of physical chemistry! Perhaps it might have been said, twenty-five years ago, that there were few good American text-books of physical chemistry, But certainly, today, we have six or eight such books, any one of which will afford plenty of good grist to a professor and his class throughout a full year's milling.

Dr. MacDougall's presentation follows, "in the main, the traditional order of presentation," as stated in the Preface. The chapter headings are: I, Introduction, Atomic Theory; II, Energy and the First Law of Thermodynamics; III, The Gaseous State; IV, The Liquid State; V, The Solid State; VI, The Structure of Atoms I; VII, The Structure of Atoms II; VIII, Physical Properties and Molecular Constitution; IX, The Second Law of Thermodynamics; X, Solutions; XI, Solutions of Electrolytes; XII, Thermochemistry; XIII, Equilibrium; XIV, Heterogeneous Equilibrium and Applications of the Phase Rule; XV, Chemical Kinetics; XVI, Electrical Conductance; XVII, Equilibrium Involving Ions; XVIII, Electromotive Force; XIX, Electrolysis; XX, Photochemistry; XXI, The Colloidal State; Index of Authors and Index of Subjects.

The book is written with an easy-flowing logic and with exceptional and gratifying clarity. Many intermediate steps in the derivations and expositions, often omitted in texts of this same class, are here included to help the student (and the professor) surmount some of the more troublesome hurdles. While several of the chapters seem very full and exhaustive for an introductory course, the topics are developed and arranged in such a way as to permit an adaptation of the subject matter to the needs of several different types of students. More than usual emphasis, but not unduly so, is given to thermodynamic approach, and the Author develops the treatment in fairly gentle stages.

This text deserves to rank with the best available. Many teachers will find it suited ideally to their requirements.

Edward Mack, Jr.

The Theory of the Properties of Metals and Alloys. By N. F. Mott, M.A., F.R.S., Professor of Theoretical Physics, and H. Jones, Ph.D., Lecturer in Theoretical Physics, The University of Bristol. Oxford University Press, 114 Fifth Avenue, New York, N. Y., 1936. x + 326 pp. 108 figs. 16 × 24.5 cm. Price, $8.00.

Elektronentheorie der Metalle. (Electron Theory of Metals.) By Dr. Herbert Fröhlich, Bristol. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1936. vii + 386 pp. 71 figs. 14.5 × 22 cm. Price, RM. 27; bound, RM. 28.80.

It is ten years since Fermi and Dirac suggested the principles of statistics which are now known by their names. This decade has seen those principles applied to the electrons in metals, with a success reminding one of the preceding years when Bohr's theory of hydrogen was being extended to explain the periodic table and the line spectra of the elements. The theory of metals is still far from the complete state which atomic theory has reached; the volumes under review are the first full sized books which have been devoted to it. But it is on the way and proceeding with great vigor.

The chemist should certainly be interested in this development. Most of the elements are metals, and they prefer to behave in ways quite different from the laws of valence which the chemists have worked out. Unlike the familiar chemical compounds, the laws of metals are not simple and qualitative ones, to be perceived without mathematical labors. The theory of metals is based on wave mechanics, and unfortunately on the more difficult and involved wave mechanics; and there seems to be no short cut to understanding it. But the theory is interpreting facts at such a rate that it can hardly be neglected, even by the most practical minded, for it is likely to be the foundation of the physical metallurgy of the future. There is no use pretending, however, that either of the volumes which have just appeared is easy reading, or even possible reading for one who is not already more or less familiar with the principles of wave mechanics. They are both well and clearly written, but the mathematics cannot be escaped. The day has passed when a chemist or metallurgist is educated to discuss the foundations of his science, if he does not know modern theoretical physics. It is just as fundamental to the chemical physics of the next generation as thermodynamics was to the physical chemistry of the last.

The two books under discussion are very similar, as is natural when one notes that both originate in Bristol, where Mott and Jones are members of the staff, and Fröhlich has been a visitor. England has been rather in the lead in the last few years in the theory of metals, partly with the help of expatriated German scientists, though this country, Russia, Germany and France have all contributed. It has been a development not only of many countries but of many people, and no collection of the leading workers in the field would be complete without fifteen or twenty names at the very least. The authors of these books have all made significant contributions, however, and naturally each emphasizes to some extent his own work. Thus Mott and Jones treat alloys in a good deal of detail; they discuss carefully the various types of lattices, and the methods of predicting the crystal structure and phase diagrams of alloys; they take up the properties of the transition metals; in general, they stay rather close to physics and chemistry, with a minimum of mathematics. Fröhlich, on the other hand, covers the mathematical part of the theory with more care, but considers principally the alkali and noble metals, the simplest group theoretically, with comparatively little treatment of the other groups of metals, and almost none of alloys. The chemist is likely to find Mott and Jones' book more to his liking. But both are in general excellent and authoritative, and both can be read with profit.

Since books on the theory of metals are a novelty, it is worth while saying what these contain. Mott and Jones begin with a discussion of the thermal properties of a crystal lattice—the equation of state, specific heat, phase diagrams of alloys, and superstructure. Then follows a treatment of the motion of electrons in a crystal lattice, first in the absence of an external field, then in a field, leading to electrical conduction, dispersion and absorption of light. The theory of cohesion and metallic binding, as applied both to pure metals and alloys, follows next, after which there is discussion of electronic specific heat, magnetic properties, and detailed calculation of electrical conductivity. Probably of most interest to chemists will be the part dealing with alloys and the conditions governing their formation and properties. Fröhlich, as has been stated, does not treat these problems, but does take up a few questions, such as thermionic emission, which Mott and Jones omit. Both books are more inclusive in some respects than the article in the "Handbuch der Physik" by Sommerfeld and Bethe, the best known previous treatment of the subject, and contain a good deal of new material, principally on cohesion and optical properties, which have developed since the time of that article. Both contain many references, those given by Fröhlich being in the form of a fairly extensive, though sometimes inaccurate, bibliography. While there are a few points on which one may take issue with the points of view of both books, these are minor affairs, and of small interest to the general reader. In general, it is safe to say that the electron theory of metals is now a branch of science in the most flourishing period of its growth, and that the books of Mott and Jones and of Fröhlich are excellent guides to its present development.

J. C. SLATER

BOOKS RECEIVED

December 15, 1936–January 15, 1937

L. ERHARD, Editor. "Blätter für Geschichte der Technik." Dritter Heft. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 101 pp. RM. 3.60.

CHARLES S. GIBSON. "Essential Principles of Organic Chemistry." The Macmillan Company, 60 Fifth Avenue, New York, N. Y. 548 pp. $5.00.

JOHN READ. "Prelude to Chemistry. An Outline of Alchemy, its Literature and Relationships." The Macmillan Company, 60 Fifth Ave., New York, N. Y. 327 pp. $5.00.

WILLIAM RIEMAN, III, AND JACOB D. NEUSS. "Quantitative Analysis. A Theoretical Approach." McGraw-Hill Book Company, Inc., 330 West 42nd St., New York, N. Y. 425 pp. $3.00.

JOHN H. YOE. "Chemical Principles with Particular Application to Qualitative Analysis." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 311 pp. $2.75.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 36: Gallium." Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 100 pp. RM. 13.87.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 23, Ammonium." Lieferung 2. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 360 pp. RM. 42.25.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 37, Indium." Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 116 pp. RM. 15.75.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 59: Eisen." Teil A, Lieferung 6–7. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 254 + 214 pp. RM. 31.15 + 27.00.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 59: Eisen. Teil D. Magnetische und elektrische Eigenschaften der legierten Werkstoffe." Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 466 pp. RM. 57.75.

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

Potassium Iodide as a Primary Standard Substance in Permanganimetry

BY I. M. KOLTHOFF, H. A. LAITINEN AND J. J. LINGANE

It was shown in a previous paper from this Laboratory[1] that the potentiometric iodide–silver titration is capable of giving results accurate to within 0.02%, under the proper conditions. The purpose of the present study was to investigate the accuracy of several iodide-permanganate titration methods, with a view to using potassium iodide as a primary standard substance in permanganimetry. For this purpose we have compared the results obtained by standardizing solutions of potassium permanganate against potassium iodide, with those obtained using arsenious oxide and sodium oxalate as standard substances.

Materials

Potassium Iodide.—The potassium iodide used in this work was synthesized from purified potassium bicarbonate and pure hydriodic acid. The hydriodic acid was synthesized directly from purified iodine and hydrogen, using platinized asbestos as catalyst, in the all-glass apparatus shown in Fig. 1. All joints in this apparatus were of ground glass lubricated with a minimal amount of phosphoric acid, except the joint at the absorption bulbs, D, which was sealed with a drop of water. Iodine, purified by repeated sublimation from potassium iodide, was placed in the bulb A and volatilized by immersing the bulb in an electrically heated glycerol bath at 150 to 180°. The iodine vapor and an excess of pure hydrogen, introduced through the short arm, then passed through the porous platinized asbestos plug at B, which was heated to about 400° by a burner at the end close to the bulb while the other end was left unheated. The resulting hydrogen iodide passed through the trap C, which was immersed in a freezing ice–salt mixture to condense a small amount of unreacted iodine, and the gas was then absorbed in conductivity water in the absorption bulbs D to give a concentrated hydriodic acid solution.

Before starting a run and before the catalyst was heated, the apparatus was flushed out with nitrogen for a few minutes to prevent explosive reaction of hydrogen with oxygen from the air at the surface of the platinized asbestos. Hydrogen was then passed through the apparatus for a few minutes before the heating was started, and the rate of hydrogen flow during a run was so adjusted that about 2–3 bubbles per second escaped from the absorption bulbs. The rate of the reaction was controlled easily by regulating the temperature of the iodine bulb A and the rate of flow of hydrogen. In a typical run, 180 g. of iodine was converted to hydriodic acid in six hours with a yield better than 95%.

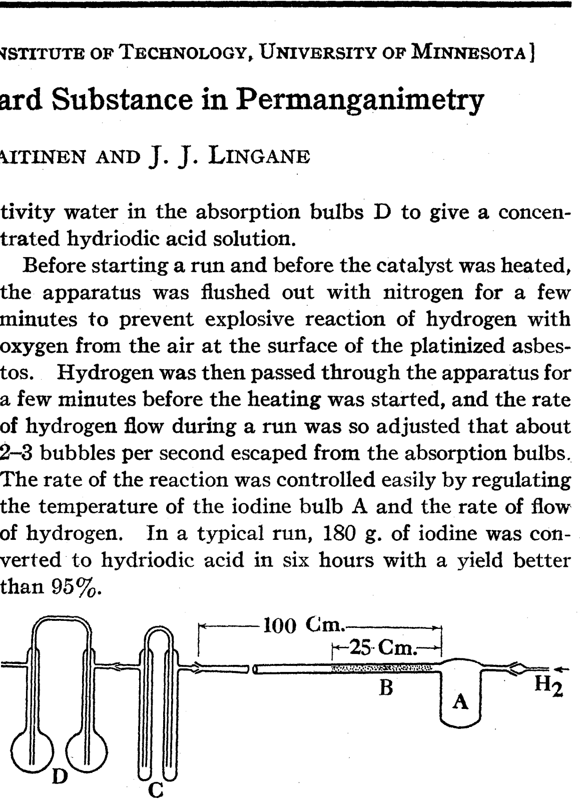

Fig. 1.—All glass apparatus for synthesis of hydriodic acid.

The hydriodic acid solution was treated with a slight deficiency of potassium bicarbonate which had been recrystallized repeatedly from water at 70° in an atmosphere of carbon dioxide, and the resulting solution of potassium iodide containing excess hydriodic acid was filtered and evaporated to crystallization on an electric hot-plate in an Erlenmeyer flask through which a rapid stream of hydrogen was bubbled. The potassium iodide obtained on cooling the solution was filtered off on a sintered glass funnel, freed from excess mother liquor by suction, and finally dried and stored in a desiccator over fused potassium hydroxide.

The salt was prepared for weighing by fusion in a platinum boat in an atmosphere of pure, dry hydrogen, under which conditions there was no trace of decomposition [1]

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(1) I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **58**, 1524 (1936).

This method of obtaining very pure potassium iodide will be described in greater detail in a forthcoming volume of "Inorganic Syntheses."

Arsenious Oxide.—Bureau of Standards arsenious oxide was dried in a desiccator over concentrated sulfuric acid to constant weight. A sample of antimony-free arsenious oxide kindly furnished by Professor Foulk[2] was dried similarly.

Sodium Oxalate.—Bureau of Standards sodium oxalate was dried to constant weight at 105°.

Potassium Permanganate Solution.—Stock solutions of potassium permanganate, approximately 0.1 and 0.4 *N*, were prepared from reagent quality potassium permanganate, allowed to stand for two weeks, and filtered through a sintered glass filtering funnel. The stock solutions were checked at regular intervals by potentiometric titration of fused potassium iodide samples. Approximately 0.01 *N* solutions were prepared by diluting weighed portions of the stock solutions in a calibrated volumetric flask. A fresh 0.01 *N* solution was prepared every five days.

Experimental Technique.—The titrations were performed by adding the major portion of the stock solution from a weight buret until an end-point was closely approached, after which the titrations were finished by the use of 0.01 *N* solution delivered from an ordinary volume buret.

Weights and volumetric apparatus were calibrated carefully by standard methods. Weighings were corrected to vacuum using the following densities: brass weights 8.4, potassium iodide 3.13, arsenious oxide 3.86, and air 0.0012 g. per cc.

1. Iodide–Permanganate Titration According to Andrews.[3]—This titration is based upon the oxidation of iodide to colorless iodine monochloride in strong hydrochloric acid medium, the end-point being determined by the use of carbon tetrachloride.

About 25 ml. of water was introduced into a 500-ml. iodine flask and about 1 ml. of concentrated hydrochloric acid was added. Pure potassium bicarbonate was added in small portions until a slight excess was present and most of the air in the flask was replaced by carbon dioxide. A weighed sample of fused potassium iodide in a platinum boat was then introduced, and after solution of the salt was complete, the platinum boat was removed by means of a suitably bent glass rod and washed thoroughly with water. Sufficient concentrated hydrochloric acid (13.3 *N*) was added to obtain the desired acid concentration at the end-point given in Table I, assuming a final volume of 325–350 ml. The solution was cooled in an ice-bath and 6 ml. of carbon tetrachloride was added. The titration was then carried out with 0.4 *N* potassium permanganate from a weight buret until within a few drops of the end-point, and then finished with the 0.01 *N* solution, the end-point being detected by the disappearance of the iodine color from the carbon tetrachloride upon thorough stirring.

The results of titrations carried out at various acidities of hydrochloric acid are given in Table I, and the normality found compared with that obtained in the standardization against pure potassium iodide according to the potentiometric method by oxidation to iodine. It will be shown later in this paper that the latter method gives exact results.

Table I

Titration of Potassium Iodide with Potassium Permanganate According to Andrews

No.	Final concn. HCl, *N*	KI (vacuum), g.	Total $KMnO_4$ soln. added, g.	Normality of $KMnO_4$, g.	Normality of $KMnO_4$ (potentiometrically)	Error of Andrews method, %
1	3.1	1.09311	28.761	0.45783	0.45753	+0.066
2[a]	3.3	1.23485	32.054	.46401	.46460	− .130
3	3.7	1.37193	36.118	.45756	.45753	+ .007
4	3.8	1.35017	35.027	.46433	.46460	− .058
5	4.3	0.99039	26.070	.45762	.45753	+ .020
6	5.1	1.09551	28.421	.46432	.46460	− .060
7	5.8	1.37068	35.564	.46415	.46460	− .097
8[a]	8.2	1.23690	32.490	.45858	.45768	+ .197
9	8.9	1.25115	32.864	.45859	.45768	+ .199
10	9.0	1.07241	28.180	.45841	.45768	+ .160

[a] Titration carried out rapidly (*ca.* 30 ml./min.). In the other cases the titrations were carried out no more rapidly than 10–15 ml./min.

2. Potentiometric Titration of Potassium Iodide by Oxidation to Iodine.—The fused sample of potassium iodide was dissolved in about 50 ml. of water in a wide-mouthed bottle. One ml. of concentrated sulfuric acid was added from a pipet, and a stream of purified nitrogen was bubbled through the solution to provide stirring. The final volume was about 100 ml., and the final sulfuric acid concentration was about 0.36 *N*. The usual potentiometric apparatus with a bright platinum indicator electrode was employed. Care was taken to wait for a steady e. m. f. after each addition of reagent. The end-point, found from the maximum value of $\Delta E/\Delta V$, could be determined with a precision of ±0.005%.

3. Titration According to the Iodocyanide Method of Lang.[4]—In this titration the iodide is oxidized to colorless iodine cyanide in dilute acid solution in the presence of hydrocyanic acid. The accurately weighed sample of potassium iodide (1 to 1.3 g.) was dissolved in an iodine flask in 25 ml. of water and 50 ml. of 4 *N* sulfuric acid and 30 ml. of 0.5 *N* potassium cyanide were added. The mixture was titrated with permanganate until near the end-point. Then 20 ml. of 0.2% starch solution was added and the titration continued with 0.01 *N* permanganate until the solution was colorless. In all titrations this end-point appeared 0.07% too early due to the fact that part of the iodine is present as iodine cyanide which is not reactive with starch and to the limited sensitivity of the iodine starch reaction. After the starch end-point had been reached, 2 drops of 0.025 *M* ferrous phenanthroline indicator were added and the titration continued until the color went from red to practically colorless. The ferrous phenanthroline must not be added before the starch iodine end-point as the indicator reacts with the iodine.

4. Titration by the Acetone Method of R. Berg.[5]—This titration is based upon the fact that the iodine first formed reacts with acetone present in the solution to give colorless iodoacetone.

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(2) See C. W. Foulk and P. G. Horton, This Journal, **51**, 2416 (1929).

(3) L. W. Andrews, *Z. anorg. allgem. Chem.*, **36**, 76 (1903); This Journal, **25**, 756 (1903).

(4) R. Lang, *Z. anorg. allgem. Chem.*, **122**, 332 (1922).

(5) R. Berg, *Z. anal. Chem.*, **69**, 369 (1926); compare also D. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **8**, 199 (1936).

Instead of using potassium iodate as recommended by Berg, potassium permanganate was used in the following titrations.

The fused sample of potassium iodide was dissolved in 25 ml. of water and 50 ml. of redistilled acetone, 20 ml. of 9 N sulfuric acid and water were added to give a volume of 200 ml. Near the end-point either 5 drops of 0.2% diphenylamine sulfonate or 2 drops of 0.025 M ferrous phenanthroline were added as indicators. The titrations were not well reproducible, indicating an average normality which was 0.55% low. For this reason the results are not tabulated. The poor results are probably due to a low rate of reaction between acetone and iodine.

5. Standardization of Potassium Permanganate with Arsenious Oxide. (a) **Potentiometrically.**—The sample of arsenious oxide (0.8 to 1 g.) was dissolved in 10 ml. of 6 N sodium hydroxide, which was free of reducing agents. Ten ml. of concentrated hydrochloric acid and 100 ml. of water were then added, the solution at the start of the titration thus being about 0.5 N in hydrochloric acid. One drop of 0.0025 M potassium iodate was added as catalyst, together with 1.0 g. of sodium chloride. The titrations with potassium permanganate were carried out using nitrogen for stirring, with care to wait for equilibrium, and the end-point determined from the maximum value of $\Delta E/\Delta V$.

(b) **Visually.**—The titrations were performed as in (a) above but with titration to the point where the first permanganate color was visible. This end-point appeared 0.012% later than the potentiometric end-point. Using ferrous phenanthroline as indicator, the end-point coincided to within 0.003% with the potentiometric end-point.

The results of the various titrations are given in a condensed form in Table II. In the last column the error in the normality is referred to the value obtained by the potentiometric iodide titration.

TABLE II

STANDARDIZATION OF 0.46 N POTASSIUM PERMANGANATE WITH POTASSIUM IODIDE AND ARSENIOUS OXIDE

No.	Standard substance	Method	Detns.	Average normality found	Av. dev. from mean, %	Diff. in normality related to (1), %
1	KI	Potentiometric	5	0.45753	±0.004	(0.00)
2	KI	Lang[a]	5	.45771	± .03	+ .04
3	As_2O_3[b]	Potentiometric	3	.45737	± .017	− .034
4	As_2O_3[c]	Potentiometric	3	.45740	± .015	− .028

[a] Ferrous phenanthroline end-point. [b] Bureau of Standards product (99.97% pure). [c] Product from Professor Foulk.

6. Standardization of Potassium Permanganate with Sodium Oxalate.—Since the procedures described for the standardization of potassium permanganate with sodium oxalate are given for 0.1 N solutions, permanganate solutions of the latter strength were prepared and standardized potentiometrically against pure potassium iodide. In the standardization with oxalate the procedures of McBride,[6] of Kolthoff,[7] and of Fowler and Bright[8] were followed closely. In all cases the end-point was found potentiometrically by finishing the titration with 0.01 N permanganate. The calculation of the results is based upon a purity of 99.96% as stated by the Bureau of Standards. The results are given in Table III.

TABLE III

STANDARDIZATION OF 0.09573[a] N POTASSIUM PERMANGANATE AGAINST SODIUM OXALATE

Method used	Differences in normality found, %				Average error
McBride	+0.31	+0.15	+0.16		+0.21
Kolthoff	+ .13	+ .05	+ .22		+ .13
Fowler and Bright	+ .09	+ .09	+ .06	+0.04	+ .07

[a] Normality determined by potentiometric titration against potassium iodide.

Discussion

1. It is known that dependent upon the acidity the results of the Andrews method may be high or low.[9] At a final acidity between 3.7 and 5.5 N the permanganate normality found was on an average 0.04% smaller than that found by the direct potentiometric titration. At the specified acidities the reproducibility is very good. At acidities between 8 and 9 N, the normalities found were about 0.2% too high, indicating that too little permanganate was used for a given amount of iodide. This may be due to an induced air oxidation of potassium iodide during titration or to a slow reaction near the end-point. It may be mentioned that a solution of potassium iodide in 7–8 N hydrochloric acid could be allowed to stand for a considerable time before an iodine color was noticed in the carbon tetrachloride layer upon shaking.

2. The potentiometric titration of iodide with potassium permanganate in dilute sulfuric acid gives exact and precise results, easily reproducible to within ±0.01%. The normality of the permanganate found by this method agreed within 0.03% with that obtained in the standardization with Bureau of Standards arsenious oxide, and with the antimony-free sample of arsenious oxide obtained from Professor Foulk. The titration of iodide according to Lang also gives satisfactory results and can be recommended with the Andrews titration for the standardization of potassium permanganate.

In order to avoid the troublesome fusion of

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(6) R. S. McBride, THIS JOURNAL, **34**, 393 (1912).

(7) I. M. Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924).

(8) R. M. Fowler and H. A. Bright, *Bur. Standards J. Research*, **15**, 493 (1935).

(9) E. H. Swift, THIS JOURNAL, **52**, 894 (1930); Swift and Garner, *ibid.*, **58**, 113 (1936); F. A. Philbrick, *J. Chem. Soc.*, 2254 (1930).

potassium iodide in a hydrogen atmosphere, experiments were performed using samples dried simply at 200–225°. The normalities obtained with the unfused salt were 0.02 to 0.03% higher than with the fused salt, indicating the retention of a very small amount of occluded water.

3. Although sodium oxalate and oxalic acid are classical primary standards, they are not suitable for the highly exact standardization of potassium permanganate solutions because of side reactions. Theoretical results can be found only by a compensation of errors. In agreement with Fowler and Bright[8] we found in the present work that McBride's procedure gives high normalities (average +0.20%), the precision of the titration being not greater than ±0.1% The procedure recommended by Kolthoff[7] gives slightly better results, although the average error was still +0.13%. The best results were obtained by Fowler and Bright's procedure, although even in this case the average error amounted to +0.07% as referred to potassium iodide. Therefore, potassium iodide and arsenious oxide fulfill the rigid requirements of primary standard substances better than sodium oxalate.

Acknowledgment.—We express our appreciation to the Graduate School of the University of Minnesota for financial aid which enabled us to do this work.

Summary

1. Potassium iodide and arsenious oxide are more suitable for the exact standardization of potassium permanganate than sodium oxalate.

2. The results obtained by the potentiometric titration of pure potassium iodide and of Bureau of Standards arsenious oxide with potassium permanganate agreed within 0.03%.

3. Potassium permanganate may be standardized against potassium iodide by Andrews' method or by Lang's method under the specified conditions. The results were accurate within 0.05%.

4. The results obtained with potassium iodide dried at 200–225° were 0.025% higher than with fused samples of the salt.

Minneapolis, Minn. Received December 10, 1936

[Contribution from the Laboratory of Liquefied Gases of the Karpov Institute for Physical Chemistry]

A Study of Acid Catalysis in Liquid Ammonia

By A. I. Shatenshtein

Brönsted's work cleared up the concept of the acid–base equilibrium in any solvent. The solvent participates together with the dissolved substance in a double buffer equilibrium

$$\text{acid}_1 + \text{base}_2 \rightleftarrows \text{acid}_2 + \text{base}_1 \qquad (1)$$

This unified point of view enables one to correlate phenomena observed in different solvents, and in particular the catalysis of solvolysis reactions in aqueous and ammoniacal solutions.

From experimental results obtained in the catalysis of sugar inversion by concentrated aqueous solutions of acids it is evident[1] that the specific catalytic activity (ratio of the reaction velocity constant to the equivalent concentration of the acid) rises (as the concentration of the acid increases) in the case of perchloric, hydrobromic, hydrochloric and nitric acids (acids given in descending order of specific catalytic activity). This ratio remains constant in a solution of trichloroacetic acid and in solutions of the weaker acids the lower the dissociation constant of the acid the lower it falls.

The sequence of acids shown corresponds to the increasing firmness with which the proton is held in the molecule of acid and at the same time corresponds (for the so-called "strong" acids) to the increase of the interionic forces in their ionized solutions.

The rise in the specific catalytic activity can be attributed[2] to the primary salt effect, which may be more correctly described as the primary auto-salt effect. This is really the influence of the field of forces of the ions surrounding the solvatized protons $(H_3O \cdot nH_2O)^+$ and the reacting molecules. The increase in the concentration of the ionized acid corresponds to an increase in the strength of the field and the decrease in the degree of solvatization of the ions.

Assuming equally complete ionization in concentrated aqueous solutions of all "strong" acids, one might expect greater catalytic activity of

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[1] A. Hantzsch and A. Weisberg, *Z. physik. Chem.*, **125**, 251 (1927).

[2] J. Brönsted and Bell, This Journal, **53**, 2478 (1931).

those acids in which the interionic forces are greatest. Actually, however, the opposite phenomenon is observed.

The contradiction may be solved by assuming that the reaction of solvolysis (of the sugar inversion type) is catalyzed, in the main, by lyonium[3] ions and that in concentrated aqueous solutions of "strong" acids one has a secondary auto-salt effect, that is to say, an unequally complete displacement of the equilibrium (1) in the direction of forming undissociated molecules of acid. This is confirmed by Raman spectra.[4]

The addition to the acid solution of a neutral salt with a common anion has the same effect on the reaction velocity as raising the concentration of the acid.[5] This confirms the applicability of the term auto-salt effect to the phenomena observed when the concentration of the acid is raised.

Thus one may take it that the change in the specific catalytic activity of aqueous solutions of acids as their concentration increases is the total result of primary and secondary auto-salt effects and depends on which of these predominates.

Assuming this view to be correct and taking into account the properties of ammonia, which is a solvent with a considerably greater affinity for the proton than water and a much lower dielectric constant, one may make a prediction with regard to the acid catalysis of the ammonolysis of organic compounds (ethers, lactones, etc.) in liquid ammonia.

Equilibrium (1) is displaced much farther to the right in solutions of acids in liquid ammonia than in water. The effect of interionic forces is much stronger in liquid ammonia than in water.

From this the following conclusions can be drawn: Reactions of ammonolysis in liquid ammonia should be catalyzed by phenols, amides and imides of acids,[6] and carbohydrates. In concentrated solutions of these acids both a primary and a secondary auto-salt effect occur. The catalytic activity of dilute solutions of ammonium salts of "strong" inorganic and "weak" organic acids should be the same and should be proportional to the analytic concentration of the solvatized protons $(\mathrm{NH_4}\cdot n\mathrm{NH_3})^+$.

When the concentration of solutions of "strong" acids is increased the secondary auto-salt effect is absent.[7] Assuming that the catalytic activity of solvatized protons increases as the field of forces of the anions becomes stronger, one may expect that a series of acids, placed in ascending order of specific catalytic activity, will be antibatic to a series of acids placed in ascending order to electrical conductivity, activity and osmotic coefficients.

The aim of the present work was to test these conclusions.

Experimental Results

The velocity of the reactions was measured by the change in the rotation of the plane of polarization of a solution in liquid ammonia. For this purpose a method was worked out for polarimetric measurements in liquefied gases at room temperature.[8] The reaction velocity constants were calculated according to the equation for a reaction of the first order.

In Table IV time is expressed in hours and in the other tables in minutes. The temperature in all cases was 20 ± 0.2°.

I. Kinetics of Ammonolysis of Santonine.—As Abkin and Medvedev[9] have shown the ammonolysis of santonine in liquid ammonia proceeds quantitatively with the formation of the amide of santoninic acid.

The reaction takes place autocatalytically. The initial value of the reaction velocity constant at 20° is about 0.0004.

A. Catalysis by Ammonium Salts.[10]—In Table I the average values of reaction velocity constants of the ammonolysis of santonine in the presence of ammonium salts are given.

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(3) Undissociated molecules of an acid can only play a minor part in the catalysis of reactions of solvolysis: the more easily they yield up a proton the greater is the probability of "lyonium" ions being formed.

(4) J. Hibben, *Chem., Rev.*, **13**, 345 (1933); R. Fonteyne, *Nature*, **138**, 886 (1936).

(5) Spohr, *J. prakt. Chem.*, **32**, 32 (1885).

(6) That solutions of these substances in liquid ammonia act as acids has been shown in numerous researches by Franklin (see E. C. Franklin, "Nitrogen System of Compounds," A. C. S. Monograph Series, 1935).

(7) M. Wolkenstein (*Acta Physicochim., U. R. S. S.*, **5**, 627 (1936)) has actually shown that in the Raman spectra of concentrated solutions of $\mathrm{NH_4NO_3}$ and $\mathrm{NH_4CNS}$ in liquid $\mathrm{NH_3}$ no frequencies are observed which could be ascribed to undissociated molecules. Of course when the concentration is increased a change in the degree of solvatization of ions, including $(\mathrm{NH_4}\cdot n\mathrm{NH_3})^+$ is possible. Between ions in ammonia solutions of organic carboxyl acids, beside electrostatic forces there are also forces of a chemical nature.[14] These would also appear to be present in concentrated solutions of inorganic acids, and this should have an influence on their catalytic activity. Owing to the lack of material this question is not discussed in the present paper.

(8) A. Schattenstein, *Acta Physicochim., U. R. S. S.*, **3**, 53 (1935).

(9) A. Abkin and S. Medvedev, *J. Gen. Chem., U. S. S. R.* (in Russian), **4**, 1402 (1934).

(10) For details see A. Schattenstein, *Acta Physicochim., U. R. S. S.*, **3**, 37 (1936).

TABLE I

REACTION VELOCITY CONSTANT OF AMMONOLYSIS OF SANTONINE IN THE PRESENCE OF AMMONIUM SALTS[11]

N	$NH_4O_2CCH_3$	NH_4Cl	NH_4Br	NH_4NO_3	NH_4I
0.01	0.0043	0.0055	0.0054	0.0053	0.0054
.03	...	.0154	.0150	.0118	.0157
.05	.0197	.0242	.0248	.0221	.0236
.10	.0419	.0492	.0466	.0433	.0412

N	NH_4ClO_4	NH_4O_2CH	$NH_4O_2CC_6H_5$	$NH_4O_2CCH_2CN$	NH_4CNS
0.10	0.0386	0.0410	0.0404	0.0428	0.0408

Table II shows the effect of adding neutral salts.

TABLE II

ACTION OF NEUTRAL SALTS

	Without salt	NaI (1 *N*)	$NaNO_3$ (1 *N*)	NaBr (1 *N*)
NH_4NO_3 (0.05 *N*)	0.0221	0.0220	0.0233	0.0291
NH_4Br (0.05 *N*)	.0248	.0235	.0265	.0300

In all cases the concentration of santonine was about 2.75 g. per 100 cc. of the solution. The reproducibility of the experiments was within 3 to 5%. As an example the following are the values for the velocity constant in one of the experiments: ($K \times 10^4$): 108, 118, 116, 115, 114, 115, 112, 114, 116, 115, 116, 114, 110, 107; average 0.0114.

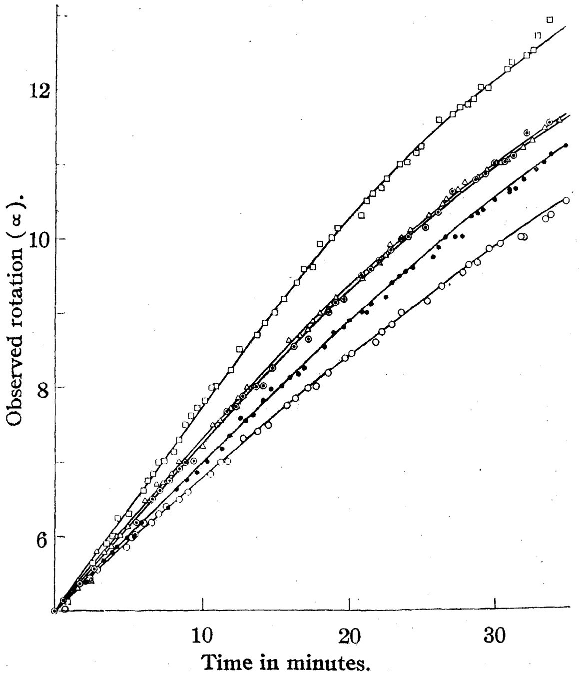

Fig. 1.—□, NH_4Cl; △, NH_4Br; ◉, NH_4NO_3; ●, NH_4I; ○, NH_4ClO_4.

B. Catalysis by Amides of Acids, etc.—Table III shows results of provisional measurements of the reaction velocity of the ammonolysis of santonine in the presence of amides of acids, phenol, etc.

TABLE III

REACTION VELOCITY CONSTANT OF AMMONOLYSIS OF SANTONINE IN THE PRESENCE OF AMIDES OF ACIDS, ETC.

Contents of table: 1, name of catalyst; 2, concentration of catalyst (moles); 3, reaction velocity constant (average); 4, calculated reaction velocity constant for a concentration of catalyst of 1 *N* (one NH_2 or OH group).

1	2	3	4
Glucose	0.49	0.0006	
Acetamide	.98	.0021	0.0021
Urea	.98	.0067	.0034
Carbazole	.44	.0024	.0055
Benzamide	.99	.0065	.0065
Cyanacetamide	.48	.0051	.0106
Phenol	.20	.0086	.0424
Formamide	1.82	.101	.0621

II. Kinetics of the Ammonolysis of Desmotroposantonine in the Presence of Ammonium Salts.[12]—It may be thought that by analogy with the ammonolysis of santonine an amide of the desmotroposantoninic acid is formed as an end-product.

Table IV gives the average values of the reaction velocity constants in the presence of 1.5-normal solutions of ammonium salts (concentration of desmotroposantonine 0.75 g. per 100 cc. of solution).

TABLE IV

REACTION VELOCITY CONSTANTS OF THE AMMONOLYSIS OF DESMOTROPOSANTONINE

N	NH_4Cl	NH_4Br	NH_4I
1.5	0.024	0.015	0.010

The reproducibility of the constants was within 5 to 10%.

III. Kinetics of the Ammonolysis of Ethyl Tartrate in the Presence of Ammonium Salts.—The reaction took place with the formation of the diamide of tartaric acid. Figure 1 gives an idea of the velocity of the reaction of the ester in the presence of a number of ammonium salts (1.02 *N*). Concentration of ester 15.2 g. to 100 cc. of solution.

Discussion of Results

The experimental material submitted confirms the propositions given above regarding acid catalysis in liquid ammonia.

From Tables I–IV and Fig. 1 it follows that as concentration increases the catalytic activity of

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[11] The last four results are provisional.

[12] For details see A. Schattenstein, *Acta Physicochim., U. R. S. S.*, **5**, 841 (1936).

ammonium salts of "strong" acids varies with the anion as follows: $ClO_4^- < I^- < NO_3^- < Br^- < Cl^-$.

In the works of Schattenstein and Uskova,[13] Gurjanova and Pleskov[14] it has been shown that the osmotic coefficients and coefficients of electrical conductivity of solutions of ammonium salts in liquid NH_3 follow in the order: $ClO_4^- > I^- > NO_3^- > Br^- > Cl^-$.

Similar data with regard to solutions of halogen salts and nitrates of alkali metals have been published in the works of Linhard[15] and Kraus.[16]

The order of catalytic activity of the amides of carboxyl acids in liquid ammonia corresponds to that of the acids themselves in water ($CH_3COOH < C_6H_5COOH < HCOOH$). There are no quite reliable data for the electrical conductivity of the amides of acids and phenols especially at great dilutions, on a basis of which one can calculate the coefficients of electrical conductivity of these solutions and corresponding dissociation constants. However, the qualitative comparison of our data with the results of Franklin and Kraus' work[17] on the whole confirm the proposition stated above.

Thus to sum up it may be asserted that the experimental material which we have hitherto been able to collect, is in good agreement with the views expressed in the present paper. This makes them quite plausible. However, further research is necessary to establish them on a firmer basis and pass from purely qualitative reasoning to stricter conclusions. Work is still in progress.

Acknowledgment.—The author wishes to thank Prof. A. M. Monossohn for his kind attention and interest in the present work.

Summary

1. The suggestion is made that the change in the specific catalytic activity of acids (including "strong" acids) as the concentration of their aqueous solutions rises is the total result of the primary and secondary auto-salt effects.

2. The conclusions are drawn as regards the acid catalysis of the ammonolysis reaction in liquid ammonia which are tested experimentally in the case of the ammonolysis of santonine, desmotroposantonine and ethyl tartrate.

3. Ammonolysis reactions in liquid ammonia are catalyzed by ammonium salts, amides of acids, phenols and carbohydrates.

4. The differences in catalytic activity of ammonium salts, both of "strong" and "weak" acids are leveled out. In dilute solutions the velocity constant is proportional to the concentration of the solvatized protons. With increase in concentration in solutions of ammonium salts of "strong" acids the antibatic nature of the series of catalytic activity and the series of electrical conductivity, activity and osmotic coefficients is observed.

5. The relationships usual in aqueous solutions of acids are observed in ammonia solutions of acids in which the proton is firmly attached (*e. g.*, the amides of acids).

MOSCOW, U. S. S. R. RECEIVED AUGUST 10, 1936

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[13] A. Schattenstein and L. Uskova, *Acta Physicochim., U. R. S. S.*, **2**, 37 (1935).

[14] E. Gurjanova and V. Pleskov, *ibid.*, **5**, 509 (1936).

[15] M. Linhard, *Z. physik. Chem.*, **175**, 438 (1936).

[16] C. A. Kraus, *J. Chem. Ed.*, **12**, 567 (1935).

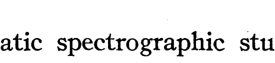
[17] E. Franklin and C. A. Kraus, THIS JOURNAL, **27**, 191 (1905).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

Notable Differences in the Absorption Curves of Certain Groups of Unsaturated Hydantoins

BY MARGARET K. SEIKEL[1]

A systematic spectrographic study of certain unsaturated hydantoins which have been synthesized in this Laboratory during the course of the past twenty years, now brings to light additional evidence for the assumption that the structural formulas commonly accepted do not serve adequately to indicate their several relationships.[2] The substances investigated are all derivatives of anisalhydantoin and, with the single exception of anisalhydantoin-N-1-acetic acid,[3] were obtained from anisalhydantoin by the direct replacement of the hydrogen atoms in the N-1- and N-3-positions. In each case the structural formulas of these substances were reported in the literature as identical with that represented above except for the fact that the hydrogen atoms in the N-1- or the N-3-position or in both were shown to have been replaced.



It now seems desirable, however, to review the data from a somewhat different angle, since a more extended study of the ultraviolet absorption spectra of a number of related compounds has made it possible to correlate consistent differences in both physical and chemical properties in such a way as to classify these compounds in separate groups. This is illustrated in Figs. 1, 2 and 3.[4] A comparison of the curves represented in Fig. 1 shows for example that the characteristic spectrum of anisalhydantoin remains almost unchanged as the result of substituting a variety of different residues for the hydrogen atom in the N-3-position. This uniformity corresponds to other similarities observed in both physical and chemical properties since all the substances whose absorption curves have been plotted, as well as other N-3-derivatives, possess many characteristics in common. For example, they all agree in being only slightly soluble in most boiling organic solvents, such as CH_3OH, C_2H_5OH, CH_3COCH_3, $CHCl_3$ and dioxane and only moderately soluble in boiling acetic acid. All represent remarkably stable compounds and have resisted every attempt to isomerize them.

On the other hand, the replacement of hydrogen in the N-1-position is accompanied by a distinct change in the absorption curve. This holds true whether the hydrogen atom in the N-3-position has been replaced or not. Here again the substitution of different groups appears to have very little effect upon the character of the absorption, as is evident from a comparison of the curves in Figs. 2 and 3. The latter represent respectively groupings of stable and labile geometrical isomers.[5] Here again the remarkable uniformity in the absorption of quite different compounds corresponds to similarities in other physical and chemical properties. For example, all dissolve readily in cold chloroform and are in general much more soluble than the corresponding N-3-derivatives so that they easily can be separated from them.[6] They are also much less stable.[7] Moreover they isomerize readily.[8]

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[1] In collaboration with Dr. Dorothy A. Hahn and Dr. Emma P. Carr.

[2] This assumption has long been the subject of informal discussion because of noticeable differences observed in the properties of two distinct groups of such compounds.

[3] This substance was prepared by condensing anisaldehyde with hydantoin-N-1-acetic acid, Renfrew and Johnson, THIS JOURNAL, **51**, 1787 (1929).

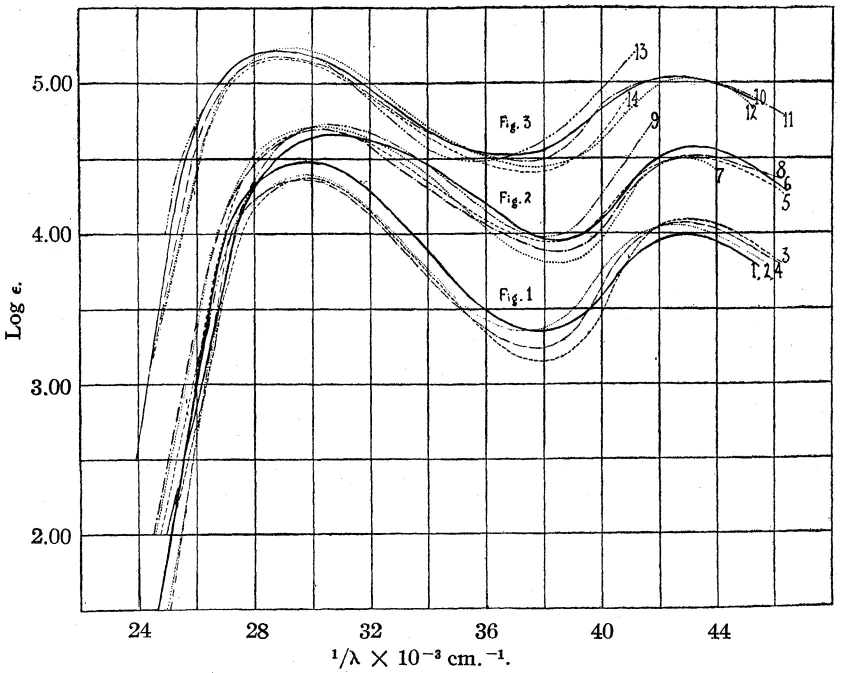
[4] Compare Figs. 1, 2 and 3 in the accompanying chart. For purposes of brevity only a few of the absorption curves which have been plotted were selected, but all which were measured fall into the same classifications.

[5] No curve for the labile isomer of 8 is given because the amount of material available at the time was not sufficient to permit the required number of recrystallizations. All substances in this group isomerize more or less in solution so that losses are sustained during the process of purification. In the case of 14 only one modification of the two possible isomers was obtained by Miss Renfrew. The fact that the absorption curve of this compound belongs obviously in this group, is of considerable importance since it, unlike all the others, contains a *free hydrogen atom* in the N-3-position.

[6] Note the relative differences in the solubilities of N-3-methylanisalhydantoin as compared with ethyl N-3-methylanisalhydantoin-N-1-acetate [Hahn and Renfrew, THIS JOURNAL, **47**, 151 (1925)] or with ethyl N-3-methyl-anisalhydantoin-N-1-phenylacetate [Hahn and Dyer, *ibid.*, **52**, 2498 (1930)]. It may be added that N-1-N-3-dimethyl-anisalhydantoin is also very soluble.

[7] They hydrolyze slowly on standing or rapidly in the presence of even traces of alkali. This is accompanied by the splitting off of groups in the N-1-position and to a lesser extent of groups in the C-5-position.

[8] In most cases the stable isomers are formed as a result of condensation reactions in an alkaline medium and are subsequently isomerized in alcohol solutions under the action of hydrogen chloride [Hahn and Gilman, THIS JOURNAL, **47**, 2953 (1925)]. In the case of 14 condensation in an acid medium resulted in formation of the labile modification. While the latter was the only compound which was separated from the reaction mixture, the fact is significant that only very low percentage yields were obtained since equilibrium mixtures of any two isomers frequently form oils and are then extremely difficult to separate.



All three groups of curves have been plotted on the same coördinates but in order to facilitate their comparison by representing all on one plate, the curves grouped in Figs. 2 and 3 have been raised 1 and 2 spaces, respectively. The values given for log ε therefore apply only to the curves grouped in Fig. 1.

Fig. 1.—Anisalhydantoin and its N-3-substituted derivatives: 1, anisalhydantoin, $NHCOCHCOC{=}CHC_6H_4OCH_3$, m. p. 243–244°[a]; 2, N-3-methyl-5-anisalhydantoin, $NHCON(CH_3)COC{=}CHC_6H_4OCH_3$, m. p. 218°[b,c]; 3, methyl 5-anisalhydantoin-N-3-acetate, $NHCON(CH_2COOCH_3)COC{=}CHC_6H_4OCH_3$, m. p. 183–184°[d]; 4, methyl 5-anisalhydantoin-N-3-propionate, $NHCON(CH(CH_3)COOCH_3)COC{=}CHC_6H_4OCH_3$, m. p. 163–164°[d].

Fig. 2.—N-1-N-3-Derivatives of anisalhydantoin, stable isomers: 5, dimethylanisalhydantoin, $N(CH_3)CON(CH_3)COC{=}CHC_6H_4OCH_3$, m. p. 91–92°[b,d]; 6, ethyl N-3-methyl-5-anisalhydantoin-N-1-acetate, $N(CH_2COOC_2H_5)CON(CH_3)COC{=}CHC_6H_4OCH_3$, m. p. 107–108°[c]; 7, methyl N-1-methyl-5-anisalhydantoin-N-1-acetate, $N(CH_3)CON(CH_2COOCH_3)COC{=}CHC_6H_4OCH_3$, m. p. 84–85°[d]; 8, methyl N-1-methyl-5-anisalhydantoin-N-3-propionate, $N(CH_3)CON(CH(CH_3)COOCH_3)COC{=}CHC_6H_4OCH_3$, m. p. 103–104°[d]; 9, ethyl N-3-methyl-5-anisalhydantoin-N-1-phenylacetate, $N(CH(C_6H_5)COOC_2H_5)CON(CH_3)COC{=}CHC_6H_4OCH_3$, m. p. 119–120.5°.[e]

Fig. 3.—N-1- and N-1-N-3- derivatives of anisalhydantoin, labile isomers: 10, isomer of 5, Fig. 2, m. p. 127.5–128.5°[d]; 11, isomer of 6, Fig. 2, m. p. 127–128°[c]; 12, isomer of 7, Fig. 2, m. p. 129.5–131°[d]; 13, isomer of 9, Fig. 2, m. p. 100.5–101.5°[e]; 14, anisalhydantoin-N-1-acetic acid, $N(CH_2COOH)CONHCOC{=}CHC_6H_4OCH_3$, m. p. 215° (223°[f]).

(a) Wheeler and Hoffman, *Am. Chem. J.*, **45**, 375 (1911). (b) Johnson and Nicolet, *ibid.*, **47**, 469 (1912). (c) Hahn and Renfrew, THIS JOURNAL, **47**, 149 (1925). (d) Hahn and Gilman, *ibid.*, **47**, 2959–60 (1925). (e) Hahn and Dyer, *ibid.*, **52**, 2497 (1930). (f) Renfrew and Johnson, *ibid.*, **51**, 1787 (1929).

In comparing the absorption curves of these three groups of hydantoin derivatives, the most pronounced difference is in the greater persistence of the long wave band in the case of the unsubstituted and N-3 substituted compounds (Fig. 1). This fact together with the higher intensity of the maximum of this band serves to differentiate compounds of this type from the N-1 or N-1-N-3 derivatives where the corresponding band is more shallow and the extinction coefficient of the maximum is distinctly lower. In the case of the stable isomers of the latter type (Fig. 2) the absorption curves start at very nearly the same frequency as that observed for the N-3-substituted derivatives but, in general, the maximum of the first band is shifted slightly toward the ultraviolet in the N-1 and N-1-N-3 compounds. The position of the second maximum remains practically unchanged for all three groups of compounds. The absorption curves of the labile isomers (Fig. 3) are very

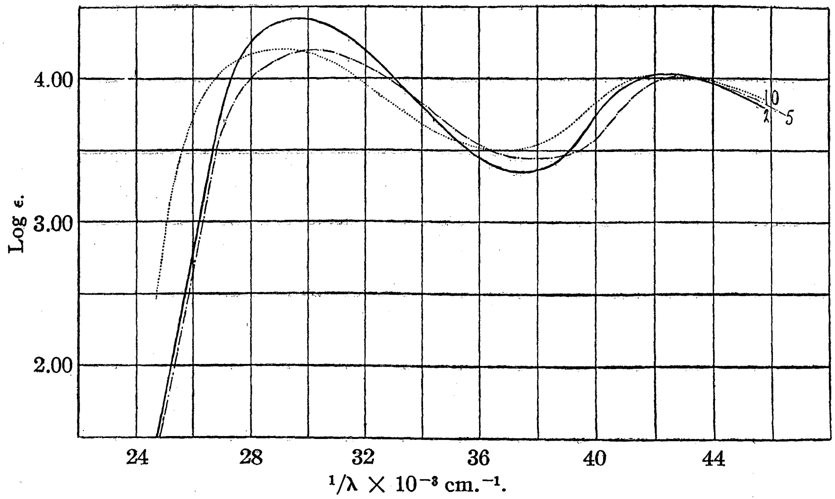
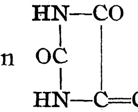


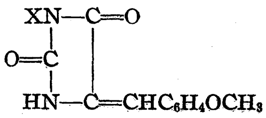
Fig. 4.—A closer comparison of: 2, N-3-methyl-5-anisalhydantoin, Fig. 1; 5, N-1-N-3-dimethyl-5-anisalhydantoin, Fig. 2; and 10, isomer of 5, Fig. 3.

similar to those of the corresponding stable modifications throughout their entire course but are shifted slightly toward the visible. These differences are so well defined that it is possible to identify a given isomer as a stable or a labile modification by means of its absorption curve. The same general relationships hold for the corresponding derivatives of benzalhydantoin  $\begin{array}{l}\mathrm{HN{-}CO} \\ \mathrm{OC} \\ \mathrm{HN{-}C{=}CHC_6H_5}\end{array}$ although the absorption curves of all of these compounds are shifted slightly in the direction of the ultraviolet.[9]

With the single exception of anisalhydantoin-N-1-acetic acid,[10] the compounds referred to in this paper were prepared in this Laboratory[11] and all were carefully recrystallized before using. The determinations of the absorption coefficients were carried out in alcohol solution by the Henri method using a Hilger quartz spectrograph (E 2), the procedure being essentially the same as that described by Hahn and Dyer.[12]

Since differences in absorption are commonly conceded to correspond to differences in molecular configuration and since the absorption of anisalhydantoin and its N-3-substitution products as a group is distinctly different from the absorption of the N-1- and N-1-N-3 derivatives, it seems probable that the two groups possess certain structural differences which are not fully indicated by the commonly accepted general formulas

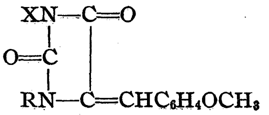
(a)



$\begin{array}{l}\mathrm{XN{-}C{=}O} \\ \mathrm{O{=}C} \\ \mathrm{HN{-}C{=}CHC_6H_4OCH_3}\end{array}$

and

(b)



$\begin{array}{l}\mathrm{XN{-}C{=}O} \\ \mathrm{O{=}C} \\ \mathrm{RN{-}C{=}CHC_6H_4OCH_3}\end{array}$

where X denotes *either* H[13] or R, and where R denotes a hydrocarbon residue. These differences may, however, be understood by assuming that *all* compounds belonging to the first group, *a*, exist chiefly in the form of their *enolic* modifications and therefore possess the molecular configuration

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[9] Unpublished work except for Hahn and Evans, THIS JOURNAL, **50**, 809–10 (1928).

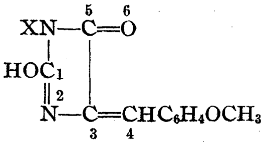
[10] Furnished through the courtesy of Renfrew and Johnson.[3] In this connection it may be noted the absorption curves of free acids are practically identical with those of the corresponding methyl and ethyl esters. For examples see Hahn and Dyer, *ibid.*, **52**, 2507 (1930).

[11] References to the methods used in the preparation of all of these substances together with their respective properties will be found in the footnotes accompanying each figure.

[12] Hahn and Dyer, THIS JOURNAL, **52**, 2511 (1930). It may be noted that the work of Hahn and Dyer was repeated for purposes of comparison and also in order to follow the absorption far enough into the ultraviolet to show the existence of the second absorption band. Eastman No. 40 and Ultraviolet Sensitive Plates were used, and a copper–silver spark. Each curve is based on at least 100 experimental points but these individual points have not been shown on the curves since they are so closely spaced as to give practically a continuous line. A relatively large number of compounds were investigated but the absorption curves of only 14 are represented. These are differentiated by numerals on the charts and in the text.

[13] Although anisalhydantoin-N-1-acetic acid, 14, was the only substance examined which contained a free hydrogen atom in the N-3-position, the fact appears to be highly significant that its spectrum is essentially the same as in cases where the hydrogen in this position has been replaced by a variety of different substituents. This would seem to indicate that the characteristic spectrum of all of these compounds is determined by the presence of a substituent in the N-1-position.

(a^1)



Molecules possessing such a configuration contain a so-called crossed conjugate system of double bonds (1-2-3-4 and 4-3-5-6) and might therefore be expected to show a selective absorption different from that of molecules containing a single conjugate system associated, as in *b*, with an isolated carbonyl group.

Summary

The absorption curves[14] together with other physical and chemical properties of anisalhydantoin and its N-3-substitution products as compared with N-1- or N-1-N-3- derivatives, serve to differentiate these substances into two separate and distinct groups. The suggestion is made that the differences between these groups may be due to corresponding differences in configuration.

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[14] For a closer comparison of the three different types of curves see Fig. 4.

SOUTH HADLEY, MASS. RECEIVED NOVEMBER 13, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

A Study of the Magneto-optic Method of Analysis

BY DONALD C. BOND

The magneto-optic method of analysis was proposed by Allison and Murphy in 1930[1] and since that time it has been used by a number of investigators, apparently with success.[2] However, there has been considerable controversy concerning the merits of the method, since many workers have been unable to duplicate the results of Allison and his co-workers. In view of the controversial status of the method, the present work was undertaken in an effort to clarify the situation.

Considerable time was spent by the author in studying the magneto-optic apparatus in use in the laboratory of Dr. T. R. Ball at Washington University, under the direction of Mr. R. E. Wingard. This equipment, which had been copied from that of Allison, was duplicated in as great detail as possible. Since it has been described elsewhere,[2] the apparatus will not be discussed further here.

After certain adjustments had been made, it was found that the Allison effect could be observed. Readings were made in the following manner. Two workers alternately observed and recorded scale readings. Every precaution was taken to prevent psychological factors from causing one scale reading to occur more frequently than another. Although it was found that the observer could seldom return to the initial scale reading or move any desired distance on the scale, even when consciously attempting to do so, nevertheless, the recorder, before each observation, moved the trolley back and forth in order to confuse the observer, finally leaving it at some random setting.

In some cases the observer desired to comment on a given reading. Thus, he might have said that it was questionable, in which case it was given a weight of one-half that of an ordinary reading. Likewise, he might have been so confident about a reading that he would want to give it a weight of two. In any case, such comments were always made *before* the scale light had been turned on and the trolley position read.

According to Allison, the "minima" for cupric chloride are found at 20.48, 20.56 and 20.68 on the scale. In Graph I (heavy line) are shown readings which were taken in the course of some work with cupric chloride solutions. All of the readings taken over a period of two months with solutions of concentration 3×10^{-12} g. of copper per cc., or greater, have been included, without any omissions. Readings taken at smaller concentrations have not been plotted because it is believed that the "minima" for cupric chloride are not present at these concentrations.

Included in this graph are several sets of readings which are known to be unreliable because it was noticed before they were taken that the line voltage was fluctuating or that the observer's eyes were tired. Although it seems that there is sufficient reason for discarding these sets, this has not been done because it might be objected that one had retained only the data which indicated the existence of an effect. Since there is

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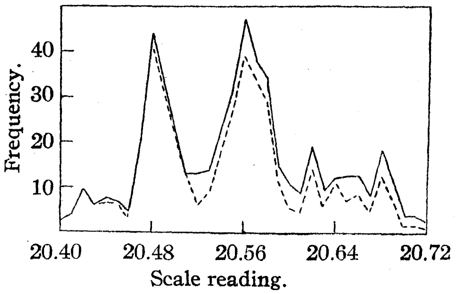
[1] Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

[2] A complete review of the work which has been done with the magneto-optic apparatus is given by Cooper and Ball, *J. Chem. Ed.*, **13**, 210 (1936).

reasonable doubt about these readings, however, they have been omitted in the dotted line in Graph I for the sake of comparison.



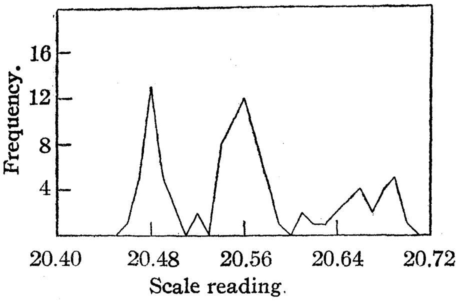
Graph I.—$CuCl_2$ "minima."

In Graph II are shown readings which were obtained with solutions of cupric chloride containing 10^{-9} g. of copper per cc. Here again all of the readings obtained with a given solution have been plotted. This graph illustrates the type of results possible with solutions whose concentrations are not near the "threshold" concentration, (these readings are included in Graph I).

The scale readings of the "minima" were found to change when the distance between the cells was changed, as reported by Allison, so that the effects observed could hardly have been caused by imperfections in the trolley system or other mechanical defects.

The magneto-optic method of analysis was applied with some degree of success to the determination of the amount of copper in a sample of phosphorescent zinc sulfide which had been prepared in these laboratories. The procedure which was used was that employed at Washington University. That is, for each solution investigated each observer moved the trolley back and forth across the position of the cupric chloride "minima" and decided whether or not the "minima" were to be seen and then the two observers compared notes. In addition, for the smaller concentrations, even in those cases in which it was thought that no "minima" could be seen definitely the scale readings of any fleeting effects observed were taken and frequency curves were plotted in the hope that these would reveal "minima" which were difficult to detect.

A number of tests were made with pure water and unknowns were run and at the time the work was done we were convinced that we could tell whether or not the "minima" were present with a given solution. In retrospect, however, it appears that there may be some doubt as to whether or not all of the insidious psychological effects possible were eliminated. While our results indicate that each Allison "minimum" is due to the presence of a certain compound, disappearing when the concentration is reduced to a very small value, we are not yet ready to say that this has been shown conclusively.



Graph II.—$CuCl_2$ "minima," 10^{-9} g. Cu per cc.

A word of apology would perhaps not be out of place here. Every paper which has appeared up to now in which the magneto-optic method has been criticized has concerned itself chiefly with the question of the reality of the "minima" observed with the apparatus. For that reason we have concentrated our efforts upon the question of the existence of the "minima," neglecting for the time a thorough investigation of the more difficult question of whether or not the "minima" disappear when the solution is diluted.

It would be difficult to say how well our observations and results compare in reliability with those of others who have worked with the Allison apparatus. Some idea of this may be obtained, however, by comparing Graphs I and II with similar graphs obtained by Ball and Crane.[3]

Miscellaneous Experiments.—A number of experiments were performed in an effort to throw some light on the behavior of the Allison apparatus and the nature of the phenomenon involved in the magneto-optic method.

A cathode-ray oscillograph was used to study the spark discharge. It was found that for each cycle of the 60-cycle a. c. supply from one to ten discharges occurred, depending upon the capacitance, voltage and gap width used. This is in agreement with the results which Cooper and Ball[2] obtained by another method. Any slight irregularity in the spark discharge is easily detected in the oscillograph, so that it is possible to obtain a much steadier discharge than by the ordinary methods. For this reason it is hoped that the oscillograph will prove a valuable accessory in the adjustment of the Allison apparatus.

A number of photographs of the magnesium spark spectrum were taken, using the color filters employed in the Allison apparatus. It was found that two lines appear, of

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(3) Ball and Crane, THIS JOURNAL, **55**, 4860 (1933).

about equal intensity. They are: a doublet having a wave length of 4481 Å. and a triplet whose average wave length is about 3830 Å. This result contradicts that of Cooper and Ball,[2] who found that only the 4481 Å. line passed through the filters.

The "Landolt fringe"[4] was found to be present in the Allison apparatus. Probably it is to be observed in any similar apparatus, although it has not been noticed by other workers, so far as can be learned.

When a cell filled with carbon disulfide is placed in one of the solenoids in the Allison apparatus and the solenoid is disconnected, the light from the spark can be completely extinguished by rotating the analyzer to the proper position. However, if the solenoid is connected in the condenser circuit so that the pulse from the spark passes through it, there is no setting of the analyzer for which the light is completely extinguished. That is, for the position of the analyzer which gives the most complete extinction possible, there is still a definite and unmistakable amount of light to be seen. Although this effect is no doubt to be observed in any Allison apparatus, so far as can be learned it has never been mentioned and there has been no speculation as to its cause.

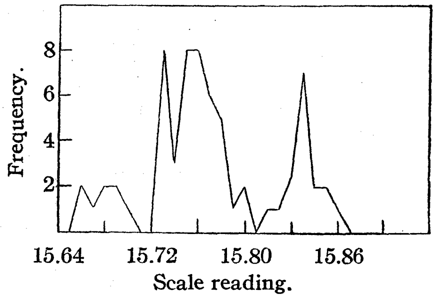
This effect may be explained as follows. The passage of the electric pulse through the solenoid around the carbon disulfide cell causes a Faraday rotation of the plane of polarization of the light passing through the cell. However, the amount and direction of this rotation vary with the time, so that there is no setting of the analyzer for which the light is completely extinguished at every instant. Since the eye integrates the illumination received by it, the net effect is that light is observed at all possible settings of the analyzer.

When a carbon disulfide cell is placed in each solenoid in the apparatus, the following may be observed. If the polarities of the solenoids are in the same direction, the effect described above is greatly increased, while if the polarities are opposed, it is possible to extinguish the light completely by rotating the analyzer to the proper angle. This is, of course, what is to be expected if the above explanation holds.

It will be shown later that there is reason for believing that the light which passes through a single carbon disulfide cell in the Allison apparatus is elliptically polarized. Tests for the presence of elliptically-polarized light were made with a quarter-wave plate, a Brace half-shade,[5] and a Bravais ellipticity half-shade,[6] but none gave any definite results. Since the double refraction expected would be at a maximum in certain quadrants of the cell, the ellipticity tests were repeated on light which passed through these quadrants, without any definite, positive results. It is not surprising that these tests failed, since the double refraction anticipated probably would be as difficult to detect as the Allison phenomenon itself.

Attempts to detect a heating effect in the carbon disulfide cell in the apparatus were unsuccessful. It was estimated that any rise in temperature due to the pulsating field present in the carbon disulfide is less than 0.001° per minute.

Observations were made with the polarity of one of the solenoids in the apparatus reversed and also with the analyzer rotated so that the Nicols were uncrossed. Definite evidence was found for the presence of effects which were located at the same trolley positions as those at which "minima" were ordinarily observed (Graph III). Although Allison, Christensen and Waldo[7] report that either maxima or minima of light intensity may be observed, according to the direction of the magnetic field and the position of the analyzer, we were unable to detect any difference between the appearances of the two phenomena. Considering the intangible character of the effect observed and the very great difficulty of even detecting it, one wonders whether it is possible for anyone to determine definitely whether it is an increase or a decrease in intensity.



Graph III.—HCl "minima," Nicols crossed, fields assisting.

Theoretical Discussion of the Allison Effect

Although the Allison effect was discovered almost ten years ago, the only explanation for it which has been advanced is the original hypothesis of Allison that it is caused by a differential time lag in the Faraday effect. Allison and his co-workers have performed a large number of experiments designed to test the theory of a Faraday time lag and their results support this hypothesis to a certain extent. However, there are several reasons why it is believed this theory is untenable.

In the first place, there is the fact that the results of Abraham and Lemoine[8] contradict this explanation. These results, obtained in a perfectly straightforward method, showed that any time lag in the Faraday effect for carbon disulfide must be less than 10^{-8} second. Allison has found time lags which are less than that of carbon disulfide by more than 10^{-8} seconds, indicating that the lag for carbon disulfide is greater than this.

In the second place, if the effect were due to a time lag in the Faraday rotation, it seems that it would be impossible to observe "minima" with the Nicols uncrossed, as they are actually ob-

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(4) R. W. Wood, "Physical Optics," 2d ed., The Macmillan Company, New York, 1911, p. 301.

(5) Brace, *Phys. Rev.*, **18**, 70 (1904).

(6) Tronstad, *J. Sci. Instruments*, **11**, 144 (1934).

(7) Allison, Christensen and Waldo, *Phys. Rev.*, **40**, 1052 (1932).

(8) Abraham and Lemoine, *Compt. rend.*, **130**, 499 (1900).

served, for the following reason: the rotation which takes place, if any, when the position of a "minimum" is passed must be very small indeed, since the effect is so difficult to observe. Mr. Wingard[9] suspects that a rotation of the plane of polarization of about ten minutes may be detected when an Allison "minimum" is passed, although this has not been established definitely. Now if the analyzer were set ten minutes off the position of extinction, a rotation of ten minutes toward the position of extinction might possibly be detected, since one would be observing the difference between an intensity of $I_0 \cos^2 (90° - 10')$, or $I_0 \sin^2 10'$, and an intensity of zero. (I_0 equals the intensity of light with Nicols parallel.) However, in the case in which the Nicols were parallel, as one moved past the position of a "minimum," he would have to detect a difference between I_0 and $I_0 \cos^2 10'$; that is, a difference of $I_0 (1 - \cos^2 10')$. But $(1 - \cos^2 10')$ is equal to 4.1×10^{-6}, so that a change in relative intensity of about 4.1×10^{-4} per cent. would be expected and this could hardly be detected. The fact is, of course, that an effect is observed under these conditions.

On the other hand, it can be shown in a similar manner that if the Allison phenomenon were caused by a rotation large enough to produce a perceptible effect with the Nicols uncrossed, then the effect obtained with the Nicols crossed should be extremely easy to detect, whereas the fact is that it is very difficult to detect.

There is still another objection to the theory that the Allison effect is caused by a Faraday time lag. If the phenomenon were caused by such a lag in rotation, then for a certain angular setting of the analyzer, near the angle of extinction, it would be expected that no effect would be observed, while at angles to one side of this position "minima" should be observed and at angles on the other side of this position "maxima" should be seen. However, experimentally it has been found possible to observe effects, indistinguishable from one another, with the analyzer set at the angle of most complete extinction or at any position on either side of this angle, within certain limits.

It is possible that a rotation of the plane of polarization takes place in the Allison apparatus when the trolley is moved past the position of a "minimum." It is even possible that this rotation, if it does occur, which is doubtful, is caused by a lag in the Faraday effect, but it seems that such a rotation cannot explain the Allison phenomenon.

A possible explanation of the Allison effect will now be submitted which is based upon the following assumptions:

1. The rapidly changing magnetic field present in the solenoids in the Allison apparatus is accompanied by an electric field. The presence of this electric field in the liquid inside the solenoid causes the beam of plane-polarized light to become elliptically polarized, because of the Kerr electric double refraction effect.

2. Under the influence of the magnetic field the molecules of the liquid are, to a certain degree, distorted and oriented. Likewise, under the influence of the electric field the molecules undergo a distortion and an orientation which are, in general, not the same, in magnitude and direction, as the distortion and orientation caused by the magnetic field. It may be supposed that the time which is measured with the Allison apparatus is the time required for the molecules of the liquid to change from the configuration which they have when the magnetic field is at maximum to the configuration which they have when the electric field is at a maximum.

According to the theory of electro-magnetism, a changing magnetic field is always accompanied by an electric field. This fact is expressed mathematically by the vector equation[10]

$$\nabla \times \overline{E} = -\frac{\mu}{c}\dot{\overline{H}} \tag{1}$$

where $\overline{E}$ is the electric vector, μ is the magnetic permeability, c the velocity of light and $\dot{\overline{H}}$ the time rate of change of the magnetic vector. In cylindrical coördinates $\nabla \times \overline{E}$ may be written[11]

$$\begin{aligned} \nabla \times \overline{E} = \frac{\bar{\rho}}{\rho}\left[\frac{\partial E_z}{\partial \theta} - \frac{\partial(\rho E_\theta)}{\partial z}\right] \\ + \bar{\theta}\left[\frac{\partial E_\rho}{\partial z} - \frac{\partial E_z}{\partial \rho}\right] \\ + \frac{1}{\rho}\bar{z}\left[\frac{\partial(PE_\theta)}{\partial \rho} - \frac{\partial E_\rho}{\partial \theta}\right] \end{aligned} \tag{2}$$

where $\bar{\rho}$, $\bar{\theta}$ and $\bar{z}$ are unit vectors along the ρ, θ and z axes, respectively, and E_ρ, E_θ and E_z are the components of the electric intensity, $\overline{E}$, along the ρ, θ and z axes, respectively.

In the Allison apparatus let the z-vector be

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(9) Private communication.

(10) Leigh Page, "Introduction to Theoretical Physics," D. Van Nostrand Co., New York, 1928, p. 433.

(11) Max Mason and Warren Weaver, "Electromagnetic Field," University of Chicago Press, Chicago, 1929, pp. 118 and 366.

along the axis of the solenoid and let the ρ and θ vectors lie in a plane perpendicular to the axis. From reasons of symmetry, the electric field cannot be a function of θ or of z, so

$$\frac{\partial E_z}{\partial \theta} = \frac{\partial(\rho E_\theta)}{\partial z} = \frac{\partial E_\rho}{\partial z} = \frac{\partial E_\rho}{\partial \theta} = 0 \qquad (3)$$

Equation (2) then reduces to

$$\nabla \times \overline{E} = -\bar{\theta}\frac{\partial E_z}{\partial \rho} + \bar{z}\left[\frac{\partial(\rho E_\theta)}{\partial \rho}\right] \qquad (4)$$

Combining with (1), we obtain

$$\nabla \times \overline{E} = -\bar{\theta}\frac{\partial E_z}{\partial \rho} + \frac{\bar{z}}{\rho}\left[\frac{\partial(\rho E_\theta)}{\partial \rho}\right] = -\frac{\mu}{c}\dot{H} \qquad (5)$$

Now $\overline{H}$ is along the z-axis and has no component along the θ-direction, so, therefore, $\frac{\partial E_z}{\partial \rho}$ equals zero and we have the result

$$\frac{1}{\rho}\frac{\partial(\rho E_\theta)}{\partial \rho} = -\frac{\mu}{c}\left|\dot{\overline{H}}\right| \qquad (6)$$

This equation shows that there is a component of the electric vector along the θ-direction, that is, perpendicular to the radius line at any point, and that the magnitude of this component depends upon ρ and the rate of change of the magnetic field. In addition, of course, it may be a function of the time. Furthermore, it is obvious from reasons of symmetry that there can be no component of the electric vector along the ρ or the z direction.

It is reasonable to assume that this tangential electric field causes a Kerr electric double refraction to take place. That is, the liquid in the solenoid acts like a peculiar kind of doubly-refracting crystal in which the optic axis is at all points perpendicular to the radius line. This is illustrated in Fig. 1, where the circle represents the cross section of the cell and the arrows represent the optic axis at various points. Regardless of the question of whether there is an Allison effect, or, if so, what its cause may be, it seems that the double refraction described above should occur in the Allison apparatus.

According to assumption number two made above, the Allison effect is a measure of the time required for the molecules of the liquid to change from the configuration which they have in a magnetic field to that which they have in an electric field. Let this time be t_{CS_2} and t_{HCl} for carbon disulfide and hydrogen chloride, respectively. Further, let the time required for the light to pass from the carbon disulfide to the hydrogen chloride cell be t_0. Then suppose that at zero time one half of one of the divided pulses reaches the solenoid around the carbon disulfide, so that at a time, t_{CS_2}, a Kerr double refraction takes place in the carbon disulfide. This would cause a certain amount of light to pass the crossed Nicols. Suppose that the wire path lengths are such that the other half of the same pulse reaches the hydrogen chloride cell at a time, $t_0 + (t_{\mathrm{HCl}} - t_{\mathrm{CS}_2})$. Then the Kerr double refraction in the hydrogen chloride would act on the same light which was elliptically polarized in the carbon disulfide by the other half of the pulse.

If the magnetic fields were assisting and the Nicols crossed, this would cause an increase in the light intensity, since the double refraction would be increased, so that maxima should be observed at this scale reading. If the magnetic fields were opposing, the effect would be the same, for the direction of the optic axis in the doubly-refracting liquid would be unchanged. Further, these same results should be obtained whether the analyzing Nicols were set at extinction or on either side of the angle of extinction.

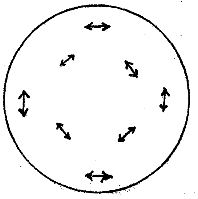

Fig. 1.

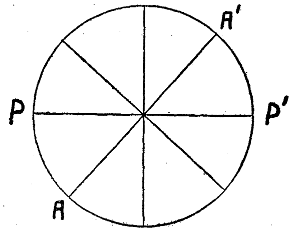

Fig. 2.

If the Nicols were parallel, or approximately so, an increase in double refraction would decrease the intensity of the light passing the analyzer. It is easily seen that in this case minima of light intensity should be observed with the magnetic fields either opposed or in the same direction, for in either case the double refraction of the hydrogen chloride would reinforce that of the carbon disulfide.

Now the effect of the double refraction would be zero in those parts of the field of vision for which the axis of the polarizer was either parallel or perpendicular to the optic axis in the carbon disulfide cell. Likewise, no elliptically polarized light would be produced in those parts of the field for which the axis of the analyzer was either parallel or perpendicular to the optic axis in the carbon disulfide. Thus, if the axis of the analyzer made an angle of 45° with that of the polarizer, the conditions would be represented by Fig. 2, where the circle is the field of view, and PP′ and AA′ are the optical axes of the polarizer and analyzer, respectively. The areas between the lines represent areas in which elliptically polarized light would be expected. It is obvious that under such conditions the double refraction would have its smallest value and it might be so small that it could not be observed. This is in agreement with the fact,[12] which is inexplicable according to the hypothesis of a Faraday lag, that the "minima" have been observed to disappear when the analyzing Nicol is rotated from the position for which it is parallel to the polarizer.

Allison, Christensen and Waldo[7] have described some experiments with the magneto-optic apparatus in which solutions possessing zero magnetic rotation were used. According to their interpretation the results indicated the presence of a Faraday time lag, but it is obvious that they may also be explained by assuming that double refraction takes place in the Allison apparatus.

Acknowledgment.—This work was suggested by Dr. Herman Schlundt and was carried out under his direction. His intense interest in the problem and his many years of careful investigation have been a continual source of inspiration.

The members of the Physics Department of the University of Missouri, particularly Dr. H. M. Reese, have constantly contributed advice, encouragement and criticism. The extent of their aid has been so great that it may be said that this is a joint production of the Physics Department and the Chemistry Department, although the Physics Department reserves judgment as to the reality of the Allison effect.

Sincere thanks are due to Mr. Perry L. Bidstrup for making many of the observations and aiding in the performance of some of the experiments.

The author also wishes to thank Dr. T. R. Ball and R. E. Wingard of the Chemistry Department of Washington University for extending the use of their laboratory and for giving so freely of their valuable information and advice.

Summary

Definite evidence has been presented for the existence of an objective effect in the Allison apparatus. Results have been obtained which indicate that this effect is caused by the presence of a particular compound, vanishing when the concentration of the compound is reduced to a very small value. However, the latter has not been proved conclusively.

Certain experiments have been described which give some information about the properties of the magneto-optic apparatus.

A partial theoretical explanation for the Allison effect has been presented.

Columbia, Mo. Received November 5, 1936

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[12] Bishop and Dollins, This Journal, **54**, 4585 (1932).

[Contribution from the Chemistry Department of the University of Melbourne]

Atomic Radii from Parachor Data and from Electron Diffraction Data

By N. S. Bayliss

Introduction

Although the parachor[1] is the most nearly additive of all "additive" properties of liquids, it has always suffered from the lack of a clear physical interpretation. Sugden, the discoverer of the function, considers it to be a measure of molecular volume, but this interpretation has been disputed by others.[2] Attempts at a theoretical treatment[3] of the parachor have not succeeded in supplying an interpretation, and without a considerable advance in our knowledge of the theory of the liquid state, it would seem impossible to obtain one on purely theoretical grounds.

By making use of the available data on atomic and molecular dimensions, it is now possible to show that Sugden's original interpretation may be applied with marked success. It will be shown in this paper that by assuming that atomic parachor constants are a direct measure of atomic volumes, it is possible to calculate atomic radii that are in good agreement with the values obtained by the electron diffraction and X-ray methods.

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(1) (a) Sugden, "The Parachor and Valency," G. Routledge and Sons, London, 1930; (b) *J. Chem. Soc.*, **125**, 1185 (1924).

(2) (a) Ferguson, *Nature*, **125**, 597 (1930); (b) Desreux, *Bull. soc. chim. Belg.*, **44**, 249 (1935).

(3) Kleeman, *Phil. Mag.*, [6] **21**, 92 (1911); Eucken, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 340 (1933).

For the present, the discussion will be confined to molecules whose structure is simple, and that contain only quadrivalent and univalent atoms.

Atomic Parachor Constants.—From the point of view of the present problem, it is unfortunate that the literature contains several sets of atomic parachor constants,[2b,4] which differ seriously, however, only in the values assigned to carbon and hydrogen. In any derivation of atomic parachors, the fundamental constant is that of CH_2, which is found from the observed parachors of members of various homologous series. Some of the previous authors seem to have committed the error of taking the arithmetic mean of $P(CH_2)$ differences over a homologous series, a procedure that automatically cancels all the measurements except those for the lowest and highest members of the series.

It was therefore thought advisable to recalculate the fundamental constants, and it will be seen that the resulting set agrees best with the set proposed by Mumford and Phillips.[4] The linear expression $P(C_nH_{2n+2}) = nP(CH_2) + 2P(H)$ was fitted by least squares to the data on the n-paraffins,[5] with the result that $P(CH_2) = 39.92 \pm 0.04$, $P(H) = 15.4 \pm 0.1$, $P(C) = 9.1 \pm 0.2$. The other fundamental parachors that were necessary for the purpose of this paper were those of the halogens, which were calculated from the data on the n-alkyl halides[6] by the relation $P(X) = P(C_nH_{2n+1}X) - nP(CH_2) - P(H)$. The recalculated atomic constants are compared with previously recorded values in Table I, where it is seen that the only significant differences are in the values for carbon and hydrogen.

TABLE I

ATOMIC PARACHORS

Atom	Sugden	M. & P.	Vogel	Desreux	This paper
CH_2	39.0	40.0	40.3	39.9	39.92
C	4.8	9.2	11.5	8.3	9.1
H	17.1	15.4	14.4	15.8	15.4
F	25.7	25.5	..	26.1	26.4
Cl	54.3	55	..	55.0	54.6
Br	68.0	69	..	68.5	68.5
I	91.0	90	..	90.0	90.3

Atomic Dimensions of Quadrivalent Atoms.—The closeness of approach of two atoms is governed by their bond radii (denoted hereafter by r) if they are chemically bound, and by the vaguer "packing" radii (r') if they are not. The comparison of atomic parachors with atomic volumes will begin with the case of quadrivalent atoms that occupy the central position in a tetrahedral molecule. Such atoms touch only those atoms to which they are chemically bound, and since the space that they occupy is determined by their bond radii only, it will be assumed that their volume is that of a sphere whose radius is r. Adopting the well established value of $r = 0.77$ Å. for the carbon atom,[7] and assuming that the atomic parachor of carbon is a measure of its atomic volume, one obtains the relation that *one parachor unit* = 0.210 Å.[3] This relation may then be used to calculate the bond radii of other quadrivalent atoms whose atomic parachors are known, the result being shown in Table II, which includes the Pauling and Huggins[7] bond radii for comparison. The atomic parachors of the elements in question have been recalculated to conform with Table I; but the differences from the Sugden values are insignificant, except in the case of carbon.

TABLE II

Atom	Atomic parachor Sugden	This paper	Bond radius, Å. Calcd.	Pauling and Huggins
C	4.8	9.1	(0.77)	0.77
Si	25.0	26.2	1.10	1.17
Ti	45.3	44.1	1.30	1.22[c]
Ge	37.4[a]	36.0	1.22	1.22
Sn	57.9	55.4	1.41	1.40
Pb	76.2	75.6	1.56	1.46
Te	..	56.7[b]	1.42	1.32[d] 1.37[e]

[a] Sidgwick and Laubengayer, THIS JOURNAL, **54**, 948 (1932). [b] Singh and Krishen, *J. Ind. Chem. Soc.*, **12**, 711 (1935). [c] Calculated from Wierl, *Ann. Physik*, **8**, 521 (1931), assuming that r for Cl = 0.99 Å. [d] Tetrahedral radius. [e] Covalent bond radius.

The agreement between the two sets of bond radii is good, but becomes better when some individual cases are considered in detail. It has been shown recently that in the chlorides and fluorides of certain quadrivalent atoms, the observed bond distances are less than those calculated from the Pauling and Huggins bond radii,[8] whereas the corresponding tetraalkyl compounds have been found to behave normally.[9] This behavior is reflected in the parachors, since the atomic parachors of silicon, germanium and tin are lower in their tetra-

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[4] Sugden, ref. 1a, p. 181; Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929); Vogel, *ibid.*, 333 (1934).

[5] Brit. Assoc. Advancement Sci. Report, 1932, p. 264. Unless indicated otherwise, all parachor data quoted in this paper will be taken from this report.

[6] For data on n-alkyl fluorides, see ref. 2b.

[7] Pauling and Huggins, *Z. Krist.*, **87**, 205 (1934).

[8] Brockway and Wall, THIS JOURNAL, **56**, 2373 (1934); Brockway, *ibid.*, **57**, 958 (1935).

[9] Brockway and Jenkins, *ibid.*, **58**, 2036 (1936).

halides than in their tetraethyls. Bond radii calculated for these elements from the parachors of their tetrachlorides and their tetraethyls are given in Table III, and are compared with the bond radii obtained from similar compounds by the electron diffraction method.[8,9] A simplification has been made in making the central atom of the tetrahedral molecule wholly responsible for the changes in both the parachor and the bond distance. The case of lead has also been included in Table III, since the bond radius calculated from the parachor is in better agreement with the value observed in lead tetramethyl[9] than with the Pauling and Huggins radius.

TABLE III

Atom	Compound	Parachor	Bond radius, Å. from Parachor	Bond radius, Å. from Electron diff.
Si	Tetraethyl	31.0	1.16	1.16[a]
	Tetrachloride	23.8	1.06	1.03
Ge	Tetraethyl	38.5	1.25	1.21[a]
	Tetrachloride	34.8	1.20	1.11
Sn	Tetraethyl	60.1	1.45	1.41[a]
	Tetrachloride	54.4	1.40	1.30
Pb	Tetraethyl	75.6	1.56	1.52[a]

[a] Values obtained from tetramethyls.

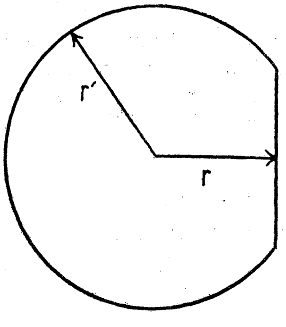

Fig. 1.—Atomic radii from parachor data and from electron diffraction data.

Atomic Dimensions of Univalent Atoms.—The volume of a univalent atom is determined largely by its packing radius, which is less easily defined than its bond radius. This case may be treated by adopting the rather naïve atomic model of a segment of a sphere (see Fig. 1) of radius r', and with the plane surface at a distance r from the center. Values of r and r' cannot both be derived from parachor data alone; but by using the relation *one parachor unit* = 0.210 Å.,[3] and by assuming the Pauling and Huggins values of r, it is possible to determine values of the packing radii of hydrogen and the halogens from their atomic parachors, as shown in Table IV. The value 1.03 Å. for hydrogen is in good agreement with those of 1.1 and 1.0 Å. quoted by Stuart,[10] and with that of 1.07 Å. observed by Pauling and Carpenter.[11] The values of the packing radii calculated for fluorine and chlorine may be compared with the following experimental values obtained by the electron diffraction method:[12] $^1/_2$(F–F) in carbon tetrafluoride = 1.12 Å., $^1/_2$(Cl–Cl) in carbon tetrachloride = 1.44 Å. and in chloroform = 1.47 Å. The results of Dornte[13] give values rather greater than the calculated packing radii of bromine and iodine, the experimental results being: $^1/_2$(Br–Br) in bromoform = 1.73 Å. and in methylene dibromide = 1.81 Å., $^1/_2$(I–I) in methylene diiodide = 2.03 Å. There is some evidence, however, that the values of Dornte are high, since Brockway and Jenkins[9] find the bond distance C–Br = 1.91 Å., which, assuming the tetrahedral angle, gives $^1/_2$(Br–Br) = 1.56 Å., and the Pauling and Huggins radii predict that C–I = 2.10 Å., which gives $^1/_2$(I–I) = 1.71 Å., in good agreement with the values in Table IV.

TABLE IV

Atom	H	F	Cl	Br	I
Packing radius, Å.	1.03	1.16	1.44	1.54	1.67

Conclusion

Although the approach to the subject has been empirical, the examples quoted above provide strong evidence that atomic parachors must be interpreted as atomic volumes. Divalent and trivalent atoms have not been included in the discussion, because of the lack of packing radius data with which to compare the atomic parachors. It is probable that many of the anomalies encountered in the study of the parachor could be explained on the basis of the above interpretation; Parachor anomalies *must* be expected in cases where there is a tendency to ionic binding or resonance, since both phenomena are accompanied by changes in molecular dimensions. It is in just such cases, unfortunately, that attempts have been made to use the parachor to determine the structure. Parachor increments due to such features as double and triple bonds find at least a qualitative explanation in the suggestion of Noyes and Singh[14] that the shorter distance between such atoms is more than compensated by their greater packing radius.

Summary

1. Revised atomic parachor constants have been calculated from existing parachor data.

2. On the assumption that atomic parachors

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(10) Stuart, "Molekülstruktur," Verlag J. Springer, Berlin, 1934, pp. 47, 48.

(11) Pauling and Carpenter, THIS JOURNAL, **58**, 1274 (1936).

(12) Pauling and Brockway, *ibid.*, **57**, 2684 (1935).

(13) Dornte, *J. Chem. Phys.*, **1**, 630 (1933).

(14) Noyes and Singh, THIS JOURNAL, **58**, 802 (1936).

are a measure of atomic volume, and that the volume of the carbon atom is that of a sphere of radius 0.77 Å., it is found that *one parachor unit* = 0.210 Å.[3]

3. By adopting simple atomic models, this relation is then used to calculate bond radii for quadrivalent atoms and packing radii for univalent atoms that are in good agreement with existing data.

MELBOURNE, AUSTRALIA RECEIVED DECEMBER 30, 1936

[CONTRIBUTION FROM THE NORTHWESTERN UNIVERSITY CHEMICAL LABORATORY]

The Specific Heats of Aqueous Sucrose Solutions at 20 and 25° and the Apparent Molal Heat Capacity of Non-electrolytes[1]

BY FRANK T. GUCKER, JR., AND FRED D. AYRES

Introduction

The specific heats of aqueous solutions of electrolytes have been studied recently by a number of investigators. The behavior of such solutions is summarized conveniently in terms of the apparent molal heat capacity. Randall and Rossini[2] first showed that over a wide range the apparent molal heat capacity is a linear function of the square root of the concentration and that the slopes of the curves increase with the valence type of the electrolyte, in qualitative agreement with the Debye–Hückel limiting law. The extrapolated value of the apparent molal heat capacity at infinite dilution is usually negative for strong electrolytes, and increasingly more negative for electrolytes of higher valence type.[3]

The apparent molal heat capacity of non-electrolytes is usually assumed to be a constant independent of concentration and nearly equal to the heat capacity of the pure solute in the liquid state. The present investigation is the beginning of a systematic study of the thermochemistry of non-electrolytic aqueous solutions, undertaken to find out how ideal these solutions are and what light they may throw on the general properties of solutions. Sucrose was chosen as the first solute because it could be obtained pure and because other thermodynamic properties of its solutions already had been investigated carefully.

Preparation of the Sucrose Solutions.—The sucrose used in these experiments was the best material obtainable, purified by the Bureau of Standards as a standard for polarimetry[4] and supplied to us through the courtesy of Dr. F. D. Rossini and Dr. F. J. Bates. Following the procedure recommended by the Bureau of Standards, the sucrose was pulverized in an agate mortar and dried for four hours at 65–70° in a vacuum of about 0.01 mm. This procedure is found to reduce the moisture content to less than 0.01%. The solutions were made up determinate, with distilled water freshly boiled to remove air. In the concentrated solutions, the sucrose and water were weighed successively into the same flask in which the solution was made up. In the dilute solutions, the smaller amounts of sucrose were determined with sufficient accuracy by weighing from a weighing bottle. All weights were reduced to the vacuum basis. In order to conserve material, the most concentrated solution (Expt. 4, Table I) was diluted quantitatively in two successive steps (Expts. $4a_1$, $4a_2$) while solution 3 was divided into two portions, each of which was diluted quantitatively to form solutions 3a and 3b.

Experimental Results.—The specific heats were determined by means of the differential twin calorimeter apparatus previously described.[5] Each value represents the average of at least two experiments with heating ratios on either side of the exact balancing ratio. The dilute sucrose solutions were handled as easily as the salt solutions, and their specific heats are probably accurate to ±0.01% as in our previous work. The great viscosity of the concentrated solutions introduced two complications which seem unavoidable in any calorimetric apparatus. First, the heat of stirring was increased enormously (amounting to about 0.001° per minute in the 5.8 m solution). This large temperature trend increased the uncertainty in determining the balancing resistance ratio to about 0.02% error in the specific heat. A second effect of the high viscosity of the solution was a lag in the distribution of heat from the coil in the working calorimeter. Heat may be lost from the working calorimeter by increased conduction up the heater lead wires, if the temperature of the heater in this calorimeter is greater than that in the tare. On the other hand, heat may be gained by the working calorimeter, because the temperature of the rest of its surface is lower than that of the tare. Fortunately these errors tend to

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[1] Parts of this paper were presented at the Midwest Sectional Meeting of the American Chemical Society at Louisville, November, 1935, and at the Group Symposium on "The Electrochemistry of Solutions" at the Kansas City Meeting of the American Chemical Society, April, 1936.

[2] Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

[3] For a discussion of this and related thermodynamic properties of electrolytes see (a) Gucker, *Chem. Rev.*, **13**, 111 (1933). For a discussion of the limiting slope, see (b) Young and Machin, THIS JOURNAL, **58**, 2254 (1936).

[4] Standard Sample No. 17. For the method of purification and specifications see "Polarimetry," Circular No. 44 of the Bureau of Standards.

[5] Gucker, Ayres and Rubin, THIS JOURNAL, **58**, 2118 (1936).

TABLE I

THE SPECIFIC HEATS AND APPARENT MOLAL HEAT CAPACITIES OF SUCROSE SOLUTIONS AT 20 AND 25°

				20°C. (in cal.$_{20}$ per degree)				25°C. (in cal.$_{25}$ per degree)			
Expt.	Wt., %	m	c(20°)	s	Φ(obsd.)	Φ(calcd.)	Δs (in 0.01 %)	s	Φ(obsd.)	Φ(calcd.)	Δs (in 0.01 %)
5	0.350	0.0103	0.0103	0.99793	140	146	−0.6	0.99793	140	151	−1.1
9	.4285	.0126	.0125	.99757	148	146	.3	.99757	148	151	−0.4
7	.6783	.0200	.0199	.99605	143	146	− .6	.99617	149	151	− .4
8	1.1184	.0331	.0328	.99343	141	146	−1.6	.99376	151	151	.0
1	1.3598	.0403	.0399	.99219	145	146	−0.4	.99240	151	151	.0
6	3.2338	.0977	.0956	.98149	146.3	146.1	.2				
2	8.3061	.2647	.2503	.95251	146.6	146.4	.5	.95376	151.7	151.5	.5
3a	19.087	.6894	.6007	.89137	147.4	147.2	1.1	.89409	152.3	152.1	1.1
3b	29.660	1.2323	.9754	.83190	148.25	148.09	1.4	.83593	152.90	152.73	1.5
3	45.275	2.4178	1.5931	.74567	149.92	149.89	0.4	.75102	153.97	153.99	−0.3
4a$_2$	52.267	3.2001	1.8973	.70769	150.81	150.90	−1.4	.71354	154.64	154.72	−1.2
4a$_1$	58.229	4.0739	2.1716	.67612	151.85	151.85	0.0	.68228	155.47	155.43	0.7
4	66.548	5.8137	2.5784	.63251	153.22	153.21	.2	.63895	156.53	156.52	.2

TABLE II

SPECIFIC HEATS, APPARENT AND PARTIAL MOLAL HEAT CAPACITIES OF SUCROSE SOLUTIONS AT EVEN MOLALITIES

	20°C. (in cal.$_{20}$ per degree)				25°C. (in cal.$_{25}$ per degree)			
m	s	$\Phi(C_{p2})$	$\bar{C}_{p2}$	$\bar{C}^{\circ}_{p1} - \bar{C}_{p1}$	s	$\Phi(C_{p2})$	$\bar{C}_{p2}$	$\bar{C}^{\circ}_{p1} - \bar{C}_{p1}$
0	1.0000	146	146	0.0	1.0000	151	151	0.0
0.5	0.9166	146.8	147.7	.0083	0.9187	151.8	152.5	.0057
1	.8551	147.70	149.42	.0309	.8586	152.45	153.64	.0213
1.5	.8081	148.53	150.92	.0647	.8125	153.03	154.70	.0451
2	.7710	149.30	152.25	.1064	.7761	153.57	155.66	.0752
3	.7165	150.66	154.38	.2012	.7222	154.54	157.25	.1463
4	.6785	151.78	155.80	.2894	.6845	155.37	158.42	.2196
5	.6505	152.67	156.50	.3459	.6567	156.07	159.17	.2797
6	.6288	153.31	156.50	.3450	.6353	156.62	159.50	.3114

cancel each other, but we have no method of measuring or calculating the resultant systematic error.

The experimental results are collected in Table I, from which no experiments are omitted. The specific heat of the 0.1 *m* solution (Expt. 6) was not determined at 25° because one of the heaters was burned out after the experiment at 20°. The experiments are numbered chronologically. Each number refers to a solution made up from weighed quantities of sucrose and water, while the letters and subscripts refer to those made by quantitative dilution in the manner already described. We have listed the weight % and molality, *m* (moles of sucrose per 1000 g. of water) taking the molecular weight of sucrose as $M_2 = 342.18$. The molarity *c* (moles of sucrose per liter of solution) at 20° was calculated with the aid of the accurate density data of the "International Critical Tables."[6] The specific heat, *s*, is relative to water at the temperature of the experiment. The values of the apparent molal heat capacity, $\Phi(C_{p2})$, calculated by means of the usual equation

$$\Phi(C_{p2}) = \left[\frac{1000}{m} + M_2\right] s - \frac{1000}{m}$$

are also expressed in calories at the temperature of the experiment. The calculated values of Φ were obtained from equations which will be described subsequently. Δ*s* is the difference, in 0.01%, between the observed values of *s* and those corresponding to the calculated values of Φ.

These results show that the apparent molal heat capacity of sucrose is not constant, but changes appreciably with concentration, although the change from 0 to 1 *m* is only about a third as great as in the case of hydrochloric acid, which has the least change of any uni-univalent electrolyte. A plot of the apparent molal heat capacity against $c^{1/2}$ shows, however, no linear relationship over any appreciable concentration range, such as that which characterizes electrolytic solutions. Instead, the apparent molal heat capacity is much more nearly a linear function of the *first* power of the concentration, although appreciable curvature appears above 1.6 molar. Figure 1 is a plot of all the values of Φ at 20°, above a concentration of 0.1 molar, comparing the two abscissas. The values at 25° are similar.

These results are almost exactly like those which Redlich and Klinger[7] found when they calculated

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(6) "I. C. T.," Vol. II, p. 343.

(7) Redlich and Klinger, *Sitzb. Akad. Wiss. Wien.*, Abt. IIb, **143**, 489 (1934); *Monatsh.*, **65**, 137 (1934).

the apparent molal volume of this same solute. Using the best density data available, they showed that the apparent molal volume is much more nearly a linear function of the first power than of the square root of the concentration, but that there is a slight concavity upward such as we find for the apparent molal heat capacity. If this functional relationship is general, it would show a clear-cut difference between the behavior of electrolytes and of non-electrolytes in solution. Very little attention has been devoted to the theory of non-electrolytic solutes, but recently Fuoss[8] has published a brief article in which he derives certain thermodynamic properties of solute molecules which may be regarded as spheres with point dipoles at the center. He finds that, in very dilute solutions, the partial molal heat capacity of such a solute should be a linear function of the first power of the concentration.

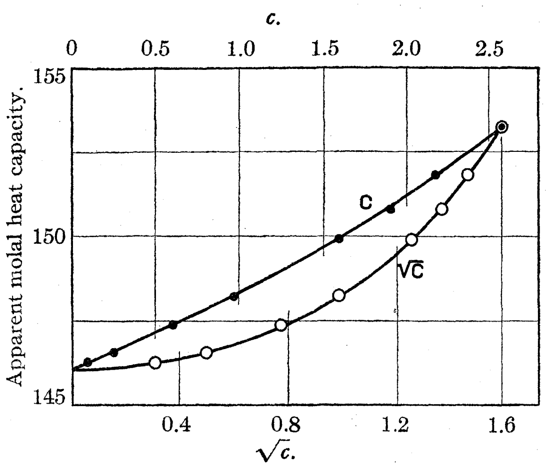

Fig. 1.—A comparison of square root and first power of concentration.

In order to obtain a convenient analytical expression for apparent molal heat capacity, which could be used to calculate values of the specific heat and partial molal heat capacities at various concentrations, we investigated plots of Φ against the molality, m, and also against ($1000\ N_2/M_1$) where M_1 is the molecular weight of the solvent and N_2 is the mole fraction of solute. N_2 is multiplied by the factor ($1000/M_1$) in order to make it equal to m in the dilute range and comparable at all concentrations. Figure 2, from which the results at concentrations below 0.1 m have been omitted to avoid confusion, shows that there is little difference between kN_2 and m, although the molarity, c, differs greatly from them both. The plot against m exhibits a curvature opposite to that against c, and about 50% greater.[9] Since the molality is a more convenient abscissa than the molarity, we employed it in subsequent calculations. A power series of the type

$$\Phi = \Phi^\circ + am + bm^2 \qquad (1)$$

proved adequate to reproduce the data over the whole range of concentration. We evaluated the coefficients by the method of least squares. Since the same error in the heat capacity makes a large change in the apparent molal heat capacity in dilute solutions and only a small change in concentrated ones, we weighted the values of Φ suitably in carrying out the calculations. The results were

$$(20^\circ) \quad \Phi = 145.87 + 1.950m - 0.1182m^2$$
$$(25^\circ) \quad \Phi = 151.20 + 1.325m - 0.0704m^2$$

From these equations we obtained the calculated values of Φ which are compared with the observed in Table I. As this tabulation shows, the agreement is quite satisfactory, with an average deviation in the specific heat of ±0.006% and a maximum deviation of 0.016%.

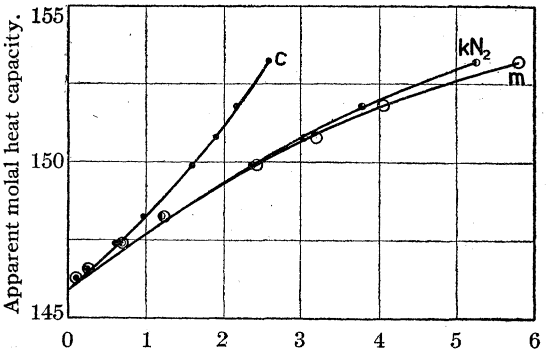

Fig. 2.—A comparison of volume and weight concentration (abscissas).

The partial molal heat capacities of solute and solvent may be calculated from equation (1) by means of the equations

$$\bar{C}_{p2} = \Phi^\circ + 2am + 3bm^2 \qquad (2)$$
$$\bar{C}^\circ_{p1} - \bar{C}_{p1} = 10^{-3}M_1(am^2 + 2bm^3) \qquad (3)$$

which are analogous to those derived by Randall and Rossini[2] when Φ is a linear function of $m^{1/2}$. For sucrose the equations are

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[8] FUOSS, THIS JOURNAL, **58**, 982 (1936).

[9] The graph of Φ against $m^{1/2}$ was also plotted. It is like an elongated S. In the dilute region it shows a curvature about midway between that of the graphs against $c^{1/2}$ and c. It nearly coincides with the latter in solutions more concentrated than 1.5 molar, although it exhibits a slight concavity downward. This curve was omitted from Fig. 1 to avoid confusion.

$$\text{(at 20° in cal}_{20}\text{/deg.)}\begin{cases}\overline{C}_{p2} = 145.87 + 3.900m - 0.3546m^2\\ \overline{C}^{\circ}_{p1} - \overline{C}_{p1} = 0.018016\,(1.950m^2 - 0.2364m^3)\end{cases}$$

$$\text{(at 25° in cal}_{25}\text{/deg.)}\begin{cases}\overline{C}_{p2} = 151.20 + 2.650m - 0.2112m^2\\ \overline{C}^{\circ}_{p1} - \overline{C}_{p1} = 0.018016\,(1.325m^2 - 0.1408m^3)\end{cases}$$

In Fig. 3 we have plotted the values of the apparent and partial molal heat capacities of sucrose at 20 and 25°. The experimental values of Φ at 20° are designated by open circles; those at 25° by dots. The values at every point agree within the limits of 0.016% in the specific heat, as we mentioned above. In the very dilute region (below 0.04 *m*) seven of the eight points lie *below* their respective lines. Although the differences appear large on the graph, only two of them actually correspond to more than 0.01% difference in *s*, as Table I shows. We hesitate to attribute any particular significance to this trend, although we hope that a study of heats of dilution of very dilute solutions, now under way in this Laboratory, may settle this question unequivocally.

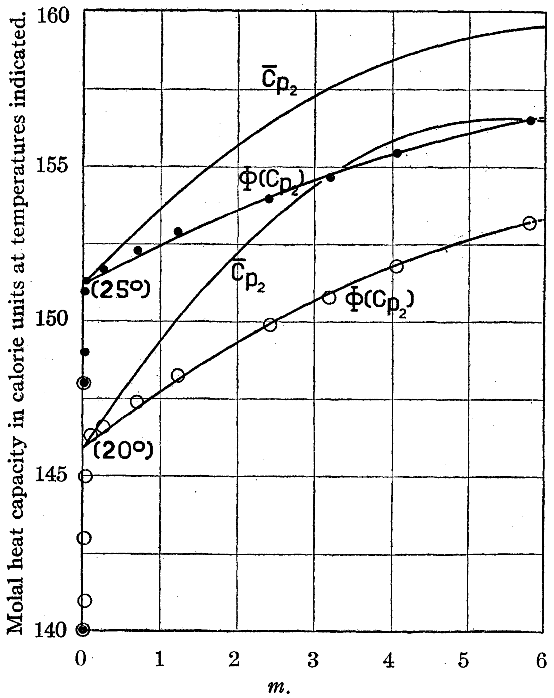

Fig. 3.—Apparent and partial molal heat capacities of sucrose at 20 and 25°.

In comparing the results at 20 and at 25°, the large change of the apparent molal heat capacity with temperature is a striking fact. The value of Φ° changes by 5.3 calorie units—over 1 unit per degree. This is much larger than the change[10] of a 1–1 electrolyte, which averages only about 0.3, and even a 2–1 electrolyte, which averages about 0.8. The initial slope of the curve is appreciably larger at 20 than at 25°. If the slope decreased at the same rate it would be 0 at about 40°—and at this temperature we might have a solute with a nearly constant apparent molal heat capacity, such as has usually been postulated for all orthodox non-electrolytes.

Comparison with Previous Results.—There are two recent series of measurements of the heat capacities of sucrose solutions. Frenzel, Burian and Haas[11] determined the heat capacities by measuring with a Beckmann thermometer the rise of temperature in the solution contained in a Dewar flask, in which a known amount of electrical energy was dissipated. They record in 15°-calories their results for solutions from 0.1 to 1 *m* at 16, 24, 32 and 39°. We have calculated the corresponding values at 20 and 25° by graphical interpolation and have converted them into 20- and 25°-calories by multiplying by the factors 1.0010 and 1.0017. These factors are obtained from Jaeger and von Steinwehr's[12] equation for the heat capacity of water at different temperatures, which Frenzel, Burian and Haas employed in their calculations. The results at 20° are given in column 3 of Table III, while the corresponding values calculated from our equation are given in the final column. Their values at 20° agree with ours to about ±0.06%, which is within their es-

TABLE III

SPECIFIC HEATS OF SUCROSE SOLUTIONS AT 20° FOUND BY DIFFERENT INVESTIGATORS

Weight, %	*m*	*s*(F., B. and H.)	*s*(Y. and A.)	*s*(I. C. T.)	*s*(G. and A.)
0	0.0	1.0000	1.0000	1.000	1.0000
	.1	0.9830			0.9810
5	.1538			0.966	.9714
	.2	.9633			.9633
	.3	.9452			.9467
10	.3247		0.9436	.930	.9428
	.4	.9305			.9312
15	.5157		.9162	.902	.9144
	.6	.9032			.9029
20	.7306			.870	.8861
	.8	.8791			.8776
	1.0	.8579			.8551
30	1.2525		.832	.811	.8299
40	1.9483		.777	.751	.7744
50	2.9224		.711	.703	.7213
60	4.3838			.677	.6668
65	5.4274		.633		.6406

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(10) Rossini, *B. S. J. Research*, **4**, 327 (1930); Gucker and Schminke, THIS JOURNAL, **55**, 1018 (1933).

(11) Frenzel, Burian and Haas, *Z. Elektrochem.*, **41**, 419 (1935).

(12) Jaeger and von Steinwehr, *Ann. Physik*, 4F, **64**, 365 (1921).

timated uncertainty of ±0.1%. Their values at 25°, on the other hand, are all *higher* than ours, on an average about 0.3%. We have no explanation for this discrepancy.

Yanovski and Archangelski[13] measured the heat capacities of solutions at approximately even weight percentages up to 65%, and at temperatures of 20.6, 51.2 and 80.8°. We have made the slight changes necessary to interpolate their results to even weight percentages at 20°, and have changed them from 15- to 20°-calories and tabulated them in column 4 of Table III. These results differ from ours on an average by ±0.4%, which is slightly more than their estimated error of 0.2 or 0.3%. Their experiments were not precise enough to detect the change of the apparent molal heat capacity with concentration and they concluded it was constant at any temperature. However, they noted its linear increase with temperature from an average value of 148.2 at 20° to 185.9 at 80°. This change is in qualitative agreement with the change in $\Phi°$ from 20 to 25°, which we have observed. The change in the *average* value is smaller because the change of the apparent molal heat capacity with temperature is less at higher concentrations.

In the fifth column of Table III we have tabulated the values of the specific heats calculated from the heat capacities given in the "International Critical Tables."[14] These represent a weighted mean of the early results. They differ from our results by ±1.5%, and are *lower* for every concentration except the last.

Other Non-electrolytes.—Unfortunately we have not been able to find in the literature any values of the heat capacities of non-electrolytes which allow us to draw further conclusions as to the functional relationship between the apparent molal heat capacity and the concentration. Such data must be accurate and they must include a series of results extending over a wide concentration range and including dilute solutions. The recent excellent study of the heat capacities of solutions of urea and mannite, made by C. M. White,[15] unfortunately does not extend above 1 *m*. White finds that "The apparent molal heat capacities seem to follow a linear equation when plotted against the $\sqrt{m}$." However, even his results, precise to ±0.01%, are not adequate to decide unequivocally between the square root and first power of the concentration over so short a range, when the change with concentration is so small.

Among the older determinations there are several series of results for liquids miscible with water, covering the whole range of concentration. We have taken the specific heat values from the "International Critical Tables" and calculated the corresponding apparent molal heat capacities of the solutes. This may introduce some errors, depending upon the way the original data were smoothed in tabulation, but it does not affect our discussion. In this case, so as to minimize the confusion of intersecting curves, we have taken the mole per cent. as abscissa and have plotted as ordinate the difference between the apparent molal heat capacity of the solute and the molal heat capacity of the pure solute (C_{p_2}). The results are shown in Fig. 4, and several interesting conclusions can be drawn. In the first place, acetone alone shows an appreciable deviation in the very concentrated solution. Most of the others lie within 10 calorie units until the solution contains 70 or more mole % water. The large deviations occur beyond this dilution, in a region which is still, how-

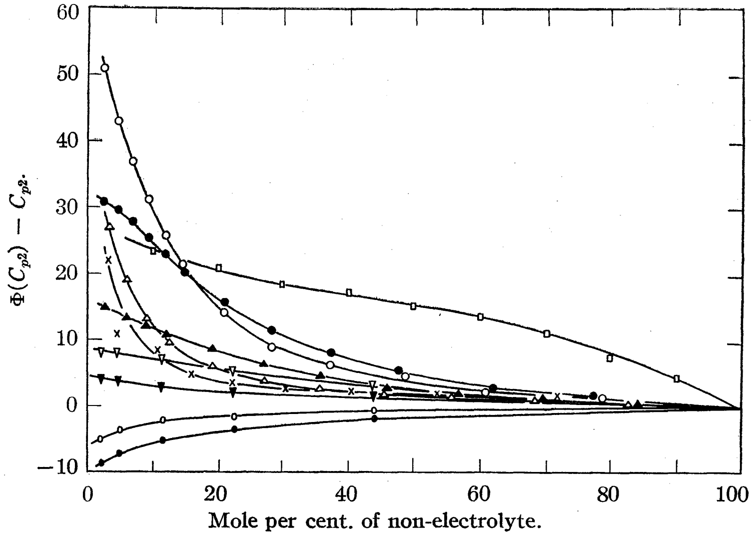

Fig. 4.—Apparent molal heat capacities of some non-electrolytes: △, methyl alcohol 5°; ▲, methyl alcohol 20°; ○, ethyl alcohol 3°; ●, ethyl alcohol 41°; 0, *n*-propyl alcohol 15°; ●, *n*-propyl alcohol 32°; ×, glycol 20°; ▽, glycerine 15°; ▼, glycerine 32°; □, acetone 20°.

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(13) Yanovski and Archangelski, *Zhur. Sakharnoi Prom.*, **2**, 614 (1928).

(14) "I. C. T.," Vol. V, p. 125.

(15) C. M. White, THIS JOURNAL, **58**, 1620 (1936).

ever, considered concentrated—8 or 10 molar. In contradiction to the behavior of all electrolytes and of sucrose, urea and mannite the apparent molal heat capacities of all these solutes except *n*-propyl alcohol *decrease* with increasing concentration. The highest value in the dilute region and the steepest slope occurs at low temperature. In other words, in almost every case when the temperature is raised, the solute shows a closer approximation to the behavior of an ideal non-electrolyte, where the apparent molal heat capacity is constant.

Acknowledgments.—It is a pleasure to express our thanks to Dr. Rossini and Dr. Bates of the Bureau of Standards for supplying us with the sucrose used in these experiments.

Summary

We have determined the specific heats of solutions of sucrose at 20 and 25° by means of a differential apparatus employing adjustable heaters.

The apparent molal heat capacity of sucrose is not constant, although it increases with concentration considerably less than a uni-univalent strong electrolyte. It is much more nearly a linear function of the first power than of the square root of the concentration. Its change with concentration decreases with rising temperature. Its limiting value at low concentration increases more rapidly with temperature than the same property of most electrolytes. The apparent molal heat capacity can be expressed satisfactorily as a second degree power series in the molality, and values of the apparent and partial molal heat capacities and the specific heats calculated by these equations are tabulated.

A review of other available specific heat data for non-electrolytes shows a general *decrease* of apparent molal heat capacity with concentration. with greater deviations at *low* temperatures.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 27, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Reactivity of Zinc Amalgams

BY HERMAN A. LIEBHAFSKY

The stability of zinc amalgams, and perhaps of most amalgams, depends in a curious way upon their concentrations. The great inertness of the concentrated (say, 1%) amalgams has been observed by all investigators who have tried to make them react with hydrochloric acid: hydrogen evolution, even when fairly strong acid is employed, does not proceed rapidly with a cold amalgam although the reaction mixture is shaken; this inertness has usually been attributed, in part at least, to the overvoltage of these amalgams for hydrogen gas. On the other hand, dilute (say, 0.001%) amalgams become increasingly unstable as their concentrations decrease, so that the electromotive forces of cells containing these amalgams vary with time and cannot be measured accurately even when the amalgams are in contact with oxygen-free zinc salt solutions.[1] That these two sets of experimental facts constitute a paradox well worth investigating appears to have escaped previous notice.

Accordingly, exploratory experiments were undertaken and the following experimental method was adopted. (1) With oxidizing agents in aqueous solution, approximately 25 cc. of amalgam and 40 cc. of solution were shaken vigorously by hand at a constant rate (240 times a minute) in a 125-cc. separatory funnel. From time to time 3-cc. samples of amalgam were withdrawn into one side of a cell containing a similar portion of the original amalgam as reference electrode in the other. The electromotive force of this concentration cell was then measured, a 1 *M* zinc sulfate–0.05 *M* sulfuric acid solution serving as electrolyte. (The acid was added in order to prevent the formation of an oxidized film on the amalgam surface; concentrations as high as 0.1 *M* have been employed without sensibly disturbing the measurements except in the case of amalgams containing less than about 10^{-4} % zinc, which are so unstable anyhow that an accurate measurement is impossible.) Beyond stirring the amalgams several times during the measurements, which were made as rapidly as possible and without excluding air, no precautions were taken. The electromo-

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[1] (a) Liebhafsky, THIS JOURNAL, **57**, 2657 (1935), recently has correlated and re-interpreted the accurate electromotive force data for zinc amalgams. See also (b) Crenshaw, *J. Phys. Chem.*, **14**, 158 (1910), and the other work cited in Ref. 1a.

tive forces were read to 0.1 mv. although this accuracy was not generally necessary. For reaction times shorter than five seconds, time was estimated from the number of times the separatory funnel was shaken. (These estimates obviously become less accurate as the reaction time decreases; perhaps the maximum inaccuracy approximates ±20%.) (2) For the experiments in Fig. 1 with oxygen as the oxidizing agent, the gas was bubbled at moderate rate through a column, initially 7 cm. high, of the amalgam contained in a test-tube; samples for the electromotive force measurements were withdrawn from its bottom by means of a pipet; the original amalgam again served as reference electrode. Under these experimental conditions the measured electromotive force shows the extent to which the amalgam being oxidized has lost zinc; and the rapidity with which the electromotive force increases with the time of reaction for an amalgam of given concentration measures the reactivity of that amalgam.

TABLE I

DETAILED RESULTS FOR 1 *N* SULFURIC ACID SOLUTIONS NEAR 25°

No.	% Zn (zero time)	Time, *t*, sec.	Milli-volts	% Zn (time *t*)	Rate = $10^4 \frac{(\Delta\% \text{ Zn})^c}{\Delta t}$
1a	0.001	1	4.0	0.000735	2.7
1b	.001	2	9.5	.000480	2.6
1c	.001	3	17.7	.000255	2.3
1d	.001	4	123	.....	2.6
1e	.001	5	1183	.....	...
2	.001	1.3	6.3	.000615	3.0
3	.001	2.5	20.1	.000212	3.4
4	.001	4.2	180	.....	(1.2)[a]
5	.001	5	1180	.....	...
8	.005	5	8.0	.0027	4.6
9	.005	10	17.0	.0013	2.8
10a	.01	5	1.7	.0088	2.4
10b	.01	10	5.1	.0068	4.0
10c	.01	15	8.6	.0051	3.4
10d	.01	20	11.9	.0040	2.2
10e	.01	30	35.8	.00063	3.4
10f	.01	40	1128	.....	(0.6)[a]
11	.01	5	5.1	.0068	6.4
12	.1	10	0.2	.0984	1.6
13	.1	30	1.6	.0883	5.0
14	1.0	10	0.0	1.0	...
15	1.0	50	1.4	0.898	20[b]

[a] Exhaustion of the zinc made a higher rate impossible. [b] This high value is probably inaccurate; the least reliable rates are those calculated from the smallest electromotive forces. When 1% amalgam was shaken for 100 sec. with 1 *N* sodium hydroxide, the average rate in the above units was $6(10^{-4})$. [c] This rate is the decrease per second in the percentage of zinc in 25 cc. of amalgam, calculated independently for each "short interval," Δt.

Figure 1 shows some of the experimental results obtained with amalgams containing 1.0 and 0.001% zinc. (Because the ordinate scale for the 1% amalgams is the larger by tenfold, the difference in reactivities is correspondingly larger than the curves alone would appear to indicate.) The oxygen gas curves are not strictly comparable with the others because of the difference in experimental method, which has been mentioned above. The curves for the dilute amalgams terminate near 1100 mv., which (as Crenshaw[1b] has discovered previously) is the electromotive force of a cell like ours when the one half-cell contains pure mercury, the other a zinc amalgam of appreciable concentration. When the electromotive force has reached this value, therefore, the complete removal of zinc from the experimental amalgam has been accomplished.

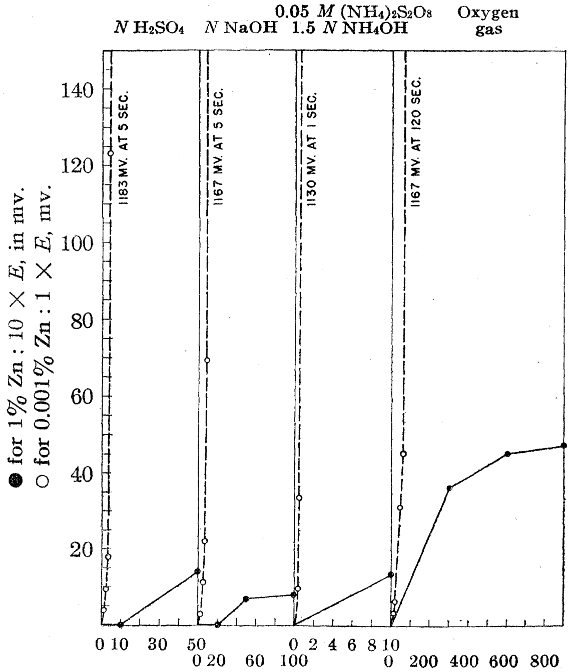

Fig. 1.

Reactivity and Concentration.—All the detailed results for amalgams of intermediate concentrations need not be reported since the curves for these concentrations fall at regular intervals between those of Fig. 1. The most important results for 1 *N* sulfuric acid are given in Table I; the rates are "short interval" values.

The conclusion to be drawn from the last column of Table I is that the rate at which zinc disappears from an amalgam shaken in air with 1 *N* sulfuric acid is virtually independent of the concentration of zinc. This conclusion is supported most strongly by the data for dilute amalgams, where the relative concentration changes are most pronounced; it shows that concentrated zinc amalgams appear to be "inert" because their absolute rate of reaction is proportionately so small as to escape detection. The results with 1 *N* sodium hydroxide closely parallel those given in Table I, and those with oxygen gas do not differ greatly. The persulfate results are the most unreproducible, because the reaction is so extremely rapid and attended by complications (temperature rise in the reaction mixture, cloudiness, scum formation); but here also the rate increases relatively little with increasing concentration of zinc; 0.001 (representing complete removal), 0.009, 0.006, 0.012%/sec./25 cc. were obtained for 0.001, 0.01 and 1% amalgams, respectively. These exploratory experiments lead to the conclusion that the absolute rate of oxidation of zinc amalgams increases only slightly with the concentration of zinc.

Air as the Oxidizing Agent.—The close parallelism of the results with 1 *N* sulfuric acid and 1 *N* sodium hydroxide suggested the investigation of intermediate acid concentrations. This investigation was restricted to the 0.001% amalgams, which were studied by the shaking method already described. The estimated times required at room temperature for the electromotive forces to reach 100 mv. (which represents almost complete removal of the zinc) in these experiments were

Solution	1 *N* NaOH	1.5 *N* NH_4OH	0.001 *N* H_2SO_4
Time, sec.	4[a]	4	6[a]

Solution	0.01 *N* H_2SO_4	0.1 *N* H_2SO_4	1 *N* H_2SO_4
Time, sec.	7	8	4 and 5

[a] Zinc hydroxide precipitated in these experiments.

These data suggest that the principal oxidizing agent for the experiments is neither hydrogen nor hydroxide ion, and probably not water. That this oxidizing agent is the oxygen of the air appears from the following results

Solution	1 *N* NaOH	H_2O	1 *N* H_2SO_4
Atmosphere	Hydrogen	Hydrogen	Hydrogen
Time, sec.	60	60	60
E. m. f., mv.	2.5	1.2	0.9

Solution	1 *N* H_2SO_4	1 *N* H_2SO_4	None (Dry)
Atmosphere	Air	Oxygen	Oxygen
Time, sec.	4	1	10
E. m. f., mv.	123	108	39

Within the accuracy of the experiments, the rate of oxidation is proportional to the partial pressure of oxygen,[2] and the reaction is less rapid when no solution is present.

Hydrogen Peroxide Formation.—Although the status of hydrogen peroxide as an intermediate step in the reduction of oxygen is so well established as to make specific reference unnecessary, the interesting work of Furman and Murray[3] deserves mention, because the reducing agent in their case was metallic mercury. To prove that hydrogen peroxide was formed also when zinc amalgam was the reducing agent, several experiments were performed with 0.01% zinc amalgam, air and 1 *N* sulfuric acid; hydrogen peroxide was identified by the formation of peroxytitanic acid and determined iodimetrically. The number of moles of hydrogen peroxide formed in these experiments was about $^1/_{15}$ to $^1/_{20}$ of the number of moles of zinc initially present, pointing either to catalytic decomposition or, more plausibly, to reduction of hydrogen peroxide by zinc. That the latter reaction occurred was proved by shaking 25 cc. of 0.01% amalgam for twenty seconds with 40 cc. of 1 *N* sulfuric acid containing 0.01 *M* hydrogen peroxide: here the zinc was completely removed, as compared with half-removal under similar conditions with the peroxide absent. $4.5(10^{-4})$ mole of zinc was oxidized, but only $3.1(10^{-4})$ of $4.0(10^{-4})$ mole of the peroxide was reduced, indicating that oxygen oxidizes some of the zinc even when hydrogen peroxide is present. These results agree with the fact that hydrogen peroxide was found at relatively low concentration when none had been added initially; in other words, hydrogen peroxide is an intermediate step in the reduction of oxygen by zinc amalgams and, under our experimental conditions, is comparable in reactivity with oxygen itself. Comparison with the work of Furman and Murray shows that

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(2) There is a chance that the results in Table I for the 1% amalgam are somewhat low because of a decrease in the partial pressure of oxygen, although the separatory funnel was opened each time a sample was withdrawn. The results with the more dilute amalgams escape this criticism since only 0.13 cc. of oxygen is required to lower the concentration of 25 cc. of amalgam by 0.001% if the oxygen is reduced to hydrogen peroxide, and nearly one hundred times that much oxygen was normally present.

Whether or not significant amounts of hydrogen gas were evolved when oxygen was reduced in the experiments with aqueous solutions is not certain. There is always the remote possibility that the reaction producing hydrogen is accelerated by the reaction between zinc amalgam and oxygen; but in the absence of concrete evidence this possibility will not be considered further. Zinc amalgams that had stood overnight in contact with the 0.05 *M* sulfuric acid electrolyte solution often showed a bubble of gas (presumably hydrogen) the next morning.

(3) Furman and Murray, THIS JOURNAL, **58**, 429 (1936).

hydrogen peroxide is far more inert than oxygen when mercury alone is the reducing agent. A complete investigation of the kinetics of these reactions must include a measurement of the concentration of hydrogen peroxide under various experimental conditions—at different temperatures, for example.

Temperature Coefficient.—For 0.1% amalgams, the following results were obtained after shaking for 120 sec.

Temperature	Near 0°	Near 30°	Near 55°
E. m. f., mv.	2.0[a]	2.1	2.1

[a] Estimated; actual results: 0.2 mv. at 80 sec.; 2.3 mv. at 160 sec.; 2.6 mv. at 240 sec.

For 0.001% amalgams, the times required at these temperatures to reach an e. m. f. of 100 mv. were estimated from the data for amalgam samples withdrawn after different times of shaking. The results were

Temperature	Near 0°	Near 30°	Near 55°
Time, sec.	6 and 7	5	5

In these measurements, the temperature was not controlled accurately; during the 0° work it rose, and during the 55° work it fell, several degrees. Nevertheless, these data show that the temperature coefficient of the reaction is near unity, and the energy barrier involved must consequently be small—perhaps three or four thousand calories.[4]

Other Oxidizing Agents.—It has been mentioned above that 40 cc. of ammoniacal 0.05 *M* (or 0.1 *N*) ammonium persulfate solution oxidized 25 cc. of zinc amalgam at a rate near 0.01%/sec.; Table I shows that the average rate for 40 cc. of 1 *N* sulfuric acid saturated with air is $3(10^{-4})$%/sec. To a first approximation, both rates are independent of the zinc concentration; with oxygen, the rate was roughly proportional to its partial pressure, hence to its concentration in solution. The concentration of oxygen in 1 *N* sulfuric acid in equilibrium with air near room temperature is about $2.2(10^{-4})M$,[5] or $9(10^{-4})N$, if the oxygen is reduced to water. The specific rate, assuming this equilibrium to be maintained under our experimental conditions, for the oxidation of zinc amalgams by dissolved oxygen will be taken as $k = 3(10^{-4})$%/sec./25 cc. amalgam/$9(10^{-4}) = 0.3$. The corresponding specific rate for ammoniacal persulfate is $0.01/0.1 = 0.1$. That two such dissimilar oxidizing agents should have virtually identical specific rates, leads to the conclusion that the reaction under investigation is essentially simple.

The results with other oxidizing agents confirm this conclusion. The experiments in Table II were carried out by the experimental method previously described, but 50, not 40, cc. of aqueous solution was usually employed. The specific rates were calculated as in the case of dissolved oxygen; an arithmetical average of the normality of the oxidizing agent was substituted for the normality of the dissolved oxygen. The results indicate that persulfate in acid solution reacts somewhat more rapidly than in ammoniacal; no great significance can be attached to this difference, however, because experimental conditions were not identical. The concentration of zinc ion in the latter solution is presumably much the lower because of the formation of the zinc-ammonia complex ion; perhaps this indicates that the rate of removing zinc ions from the amalgam, like the zinc concentration itself, has no influence on the rate of reaction. In the peroxide and permanganate experiments, a decrease in hydrogen ion concentration accompanies the oxidation of zinc; this circumstance probably complicates the permanganate results, but permanganate reactions are generally so complex anyhow that the point was not investigated further. The small and nearly constant rate observed in the experiments where persulfate and peroxide were completely consumed may be the rate at which hydrogen ion oxidizes zinc amalgam; this oxidizing agent is certainly far less reactive than the others in this group. The copper ion results are complicated by the formation of copper amalgam (the solubility of copper in mercury is about 0.002% at these temperatures).[6] The behavior of zinc amalgams toward these oxidizing agents under our experimental conditions may be summarized as follows. (1) Dissolved oxygen, hydrogen peroxide, persulfate ion, permanganate ion and copper ion oxidize zinc amalgams at about the

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[4] Since the solubility of oxygen in water decreases about 2.5-fold between 0 and 55°, there should be a corresponding decrease of rate with temperature if the heat of activation were zero. No decrease was observed, and the results of the above experiments indicate that the heat of activation is approximately large enough to counteract the decrease in solubility as the temperature is changed. On this basis, the heat of activation is about 3600 cal.

[5] Bohr, *Z. physik. Chem.*, **71**, 47 (1910). His data correspond to $10^3\alpha = 25$ for oxygen in equilibrium with sulfuric acid near 25°. The manner in which these data are cited (under "Air") in "I. C. T.," Vol. III, p. 272 ("Values of cm.^{3} of N_2 and O_2 at S. T. P. dissolved by 1 liter of soln. in equilibrium with the normal dry atmosphere") makes them liable to misinterpretation.

[6] Unpublished results from this Laboratory have confirmed published values of this datum.

same rate. (No great accuracy is claimed although the measurements are fairly reproducible.) (2) Hydrogen ion is comparatively inert, perhaps because of the difficulty of forming monatomic hydrogen.

TABLE II

ZINC AMALGAMS AND VARIOUS OXIDIZING AGENTS NEAR 25°

Time, sec.	% Zn	$10^4 \frac{(\Delta\% \text{ Zn})}{\Delta t}$	(Ox)[a]	k
1. Ammonium Persulfate in 0.1 *N* Sulfuric Acid				
0	0.0135	26	0.020	0.19
2.5	.0071	12	.007	.27
5.0	.0040	8	.002	
7.5	.0021	4	"nil"	
10.0	.0010	3	"nil"	
12.5	.0030	(1)[b]	"nil"	
15.0	"nil"		"nil"	
0	.0135	74	.040	.24
1.25	.0042	33	.021	.20
2.5	.0001	(1)	.012	
3.75	"nil"		.012	
2. Hydrogen Peroxide in Sulfuric Acid Initially 0.1 *N*				
0	0.0135	22	0.020	0.15
2.5	.0080	14	.009	.28
5.0	.0044	8	.001	
7.5	.0025	5	"nil"	
10.0	.0013	4	"nil"	
12.5	.0004	(2)	"nil"	
15.0	"nil"		"nil"	
0	.0135	55	.040	.17
1.25	.0066	38	.026	.18
2.5	.0019	(15)	.016	(.14)
3.75	"nil"		.012	
3. Potassium Permanganate in Sulfuric Acid				
0	0.0135	40	0.020[c]	0.2
2.5	.0036		"nil"	
0	.0135	93	.040[d]	.3
1.25	.0019		.016[e]	
2.5	"nil"			
4. Copper Sulfate in 0.1 *N* Sulfuric Acid				
0	0.0108	140	0.078	0.2
0.25	.0073[f]		.067	

[a] (Ox) denotes the normality of the oxidizing agent. [b] Values in parentheses may be low because of exhaustion of zinc. [c] Sulfuric acid initially 0.1 *N*. [d] Sulfuric acid initially 0.2 *N*. [e] Concentration uncertain because of oxidation of appreciable mercury. [f] This percentage was computed from the decrease, determined colorimetrically, of the copper ion concentration in the 45 cc. of solution employed. It was found that the formation of a zinc–copper amalgam made e. m. f. values unreliable for the computation of the remaining % Zn. The e. m. f. in experiments like these never reached 1100 mv., which is characteristic of pure mercury, but seemed to approach a limit near 70 mv. For the experiment above, the e. m. f. corresponded to 0.0011% zinc at 0.25 sec.

In the experiments with air as oxidizing agent, the final concentration of hydrogen peroxide was near $6(10^{-4})N$. The normality of dissolved oxygen in equilibrium with air is about $9(10^{-4})N$. The specific rate for dissolved oxygen is about 0.3; that for peroxide, about 0.2. These data agree well enough to indicate that the peroxide exists at a steady-state concentration near $6(10^{-4})N$.

The experimental data, crude though they are, permit an interesting calculation bearing on the collision number in aqueous solution. The usual calculation, in which it is assumed that the Arrhenius constant A is identical with or simply related to the collision number Z, applies to collisions within aqueous solutions; one of the underlying assumptions, which is by no means always valid, is that $k = Ae^{-Q/RT}$, where Q is the empirically determined heat of activation. We shall make a similar assumption and attempt to identify A with the number of collisions between the oxidizing agent and the amalgam surface. The calculation will be carried out for dissolved oxygen; since all the oxidizing agents investigated show comparable specific rates, the conclusions presumably are of general application. The concentration of dissolved oxygen is about $2.2(10^{-4})$ M, corresponding to a pressure of $5.5(10^3)$ dynes/sq. cm. How large will be the amalgam surface struck per second by $2.5(10^{-4})$ g. of oxygen (assumed to be unhydrated), which corresponds to removing zinc at the average rate of $3(10^{-4})\%$/sec. from 25 cc. of amalgam?

The calculation was carried out according to one equation given by Langmuir[7] and according to another given by Hinshelwood[8] with the identical result: area = 0.0032 sq. cm. The area of contact between the amalgam and aqueous solution at rest was near 15 sq. cm.; during the shaking, it was of course larger—say, 40 sq. cm. The ratio of the actual rate to the kinetic theory rate is therefore 1/12,500; if this factor is equal to $e^{-Q/RT}$, $Q = 5600$ cal., approximately. The agreement between this result and the estimate[4] $Q = 3600$ cal. is good enough to encourage confidence in the calculation; if the assumption $k = Ae^{-Q/RT}$ is valid, the sign of the discrepancy indicates either that the number of collisions is smaller than kinetic theory calls for or that the requirement of minimum energy is not alone mandatory

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(7) Langmuir, *Phys. Rev.*, **2**, 329 (1913).

(8) Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press, Oxford, 1933, p. 4.

for the occurrence of reaction on collision. The agreement indicates further (as do the facts that all oxidizing agents show nearly the same specific rate and that the rate of oxidation increases somewhat with the amalgam concentration) that the reaction does not involve diffusion through a stationary layer near the amalgam–solution interface. (Presumably a zinc amalgam at rest reacts so slowly because diffusion of reactants or resultants through a film near this interface helps limit the rate.)

Mechanism.—Any mechanism for the oxidation of zinc amalgams by oxygen (and, through legitimate inference, by other oxidizing agents) must explain the following facts: (1) the rate of oxidation is limited by the rate at which new amalgam surface is produced, other factors remaining constant; (2) the rate increases only slightly with the concentration of the amalgam; (3) it is proportional to the concentration of the oxidizing agent; (4) it is little affected by temperature changes; (5) when oxygen is reduced, hydrogen peroxide appears as a reactive intermediate compound; (6) a dry amalgam oxidizes less rapidly than one in contact with an aqueous solution.

These results are far simpler than those previously obtained in investigations of similar reactions.(9) They support the idea that we are actually studying the transfer of electrons from the amalgam to the oxidizing agent with all the usual complicating factors of a heterogeneous reaction stripped away. An attempt will now be made to formulate a mechanism describing this process, with the understanding that other mechanisms may prove acceptable provided they explain the experimental results.

The transfer of electrons to oxygen in acid solution may be visualized as follows

Rapid equilibrium: $\text{Amalgam} \rightleftharpoons \text{Amalgam surface}^{n+} + n \text{ electrons} \quad (1)$

Rate-determining: $O_2 + 2 \text{ electrons} + 2H^+ \longrightarrow H_2O_2 \quad (2)$

Rapid follow reaction: $\text{Amalgam surface}^{(n+2)+} = \text{Amalgam surface}^{n+} + Zn^{++} \quad (3)$

When the solution is not acid, it may be necessary to substitute water for hydrogen ion in reaction 2 with corresponding changes in the products. The substitution of hydrogen peroxide or of other oxidizing agents for oxygen presents no difficulty.

This mechanism, which should be applicable to many similar cases, has two necessary features: (1) the electrons transferred in reaction 2 need not originate with the zinc, but are furnished by the entire amalgam. The "electron concentration" at the amalgam surface appears to be nearly independent of the concentration of zinc; this explains why the rate does not increase more rapidly with the concentration and is in accord with the data on the electrical conductivity of zinc amalgams.(10) (2) The base-metal characteristics of zinc are responsible for the readiness with which reaction 3 proceeds. Shaking speeds up the oxidation because it continuously exposes a fresh surface, thus preventing the accumulation of reaction products, and because it provides a fresh supply of reactants. Several reasons suggest themselves for the accelerating effect of water; for example, water might make gaseous oxygen more reactive by activating it or by combining with it. The small energy barrier involved in the oxidation suggests, among other things, that the transfer of electrons to an oxidizing agent requires little or no activation when conditions are favorable.

This mechanism is conservative in that it is no more detailed than the experimental facts appear to warrant. The highly reactive substances H and HO_2, postulated by Furman and Murray, which have long been used in explaining photochemical and chain reactions(11) have not been assumed as intermediate for the following reasons. (1) It has not been proved that the reduction of oxygen by mercury or an amalgam involves a chain reaction (further experimental work bearing on this point would be welcome). (2) The assumption that H exists on a mercury or amalgam surface in contact with an aqueous solution containing an excess of reactive oxidizing agents appears implausible. (3) Intermediate products (like HO_2), to form which oxygen must accept an odd number of electrons, could scarcely have an appreciable life on a zinc amalgam surface, provided no chain or photochemical reaction is occurring. The evidence from many inorganic oxidation reactions in aqueous solutions favors the idea that oxygen is reduced to oxide in two steps (peroxide first and oxide afterward), whenever

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(9) See, for example, Fraenkel, Wengel and Cahn, *Z. anorg. Chem.*, **171**, 82 (1928).

(10) In this connection, *cf.* Schulze, *Z. Metallkunde*, **17**, 170 (1925), where data are given showing that the addition of 1% zinc to mercury increases its electrical conductivity by about 15%.

(11) See, for example, Marshall, (a) *J. Phys. Chem.*, **30**, 34 (1926); (b) THIS JOURNAL, **49**, 276 (1927); (c) Haber and Weiss, *Proc. Roy. Soc.* (London), **147A**, 332 (1934).

this is possible; in each of these steps two electrons are transferred.

There is no reason, *a priori*, why the oxidation of other amalgams—at least of amalgams baser than mercury—should not be closely analogous to the reaction under discussion. Indeed, examination of the literature reveals that the amalgams of cadmium, lead, copper, tin, thallium, sodium, potassium, lithium, calcium and barium[12] all show peculiarities of behavior indicating that their dilute amalgams are much more unstable than the concentrated.

Other Explanations.—Polymerization of zinc amalgams[1a] might serve as a qualitative explanation of the inertness of concentrated zinc amalgams, but it falls so far short of being quantitative that it must be rejected. A preferential accumulation (analogous to a Gibbs adsorption) of zinc in the surface layer of the amalgams so that the surface concentration of a very dilute amalgam is not much smaller than that of one more concentrated is another possible explanation; but it seems quantitatively unsatisfactory and conflicts with the fact that the amalgams obey the Nernst equation quite well in the concentration range $10^{-6} - 2(10^{-3})\%$.[1b] Overvoltage as a possible explanation provides little more than a restatement of the problem. The suggested explanation of Erdy-Grúz and Vázsonyi-Zilahy for the electromotive forces of cells with dilute amalgams involves several implausible features and will be examined elsewhere.

I am indebted to Dr. A. L. Marshall of this Laboratory for many valuable discussions bearing on the foregoing material.

Conclusions and Summary

The reactivity of zinc amalgams toward several oxidizing agents has been studied under experimental conditions that lead to extremely simple results. With violent agitation, the rate of oxidation for a given oxidizing agent appears to be limited mainly by the rate at which a fresh surface can be exposed; when this is constant, the rate of oxidation increases only slightly with the concentration of the amalgam, is proportional to the concentration of oxidizing agent and almost unaffected by a change in temperature. The conclusion has been drawn that the reaction being studied involves the capture of electrons by the oxidizing agent at the amalgam surface, followed by the expulsion of a zinc ion.

Work on other amalgams is required to test the generality of this conclusion. Meanwhile, the experimental facts for zinc amalgams are interesting because they show that concentrated zinc amalgams appear to be inert (although they react somewhat more rapidly than those more dilute) only because the amount of zinc disappearing from them is proportionally small enough to escape detection. Results like these have a number of applications. In the cleaning of mercury, for example, they indicate that the removal by oxidation of a metal like zinc becomes progressively easier as the concentration of zinc decreases, a situation highly unusual in purification processes.

SCHENECTADY, N. Y. RECEIVED JANUARY 6, 1937

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[12] (a) Hulett and DeLury, THIS JOURNAL, **30**, 1805 (1908); (b) Tammann and Hinnüber, *Z. anorg. Chem.*, **160**, 249 (1927); (c) Ambruster and Crenshaw, THIS JOURNAL, **56**, 2525 (1934); (d) Erdy-Grúz and Vázsonyi-Zilahy, *Z. physik. Chem.*, **177**, 292 (1936).

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

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solution. IV. The Action of Potassium and Sodium upon Silver Salts

BY WAYLAND M. BURGESS AND FRANCIS R. HOLDEN[1]

Introduction

In investigating the reducing action of the alkali metals on liquid ammonia solutions of inorganic salts, but little attention has been given to potassium as the reducing agent. Weyl,[2] in the first recorded reaction ever carried out in liquid ammonia, condensed ammonia on both potassium and a salt, using salts of zinc, copper, mercury and silver. But in later work of this kind, sodium has been employed, and a detailed description of the reactions with salts of zinc, silver and manganese has been given in previous articles of this series.[3-5] From the concept of the alkali metal solutions, as developed by Kraus,[6] one would expect the reducing action of potassium to parallel that of sodium. However, with potassium the rate of reaction with ammonia, in which the amide and hydrogen are formed, is greater. Thus, an increased tendency for the concurrent reaction between the metal and the solvent, as was observed in the reduction of manganous iodide with sodium,[5] is to be expected.

In order to compare directly the reducing action of potassium and sodium, several silver salts have been reduced by each of these metals. The reactions are found to be similar in that the silver salt is reduced to free silver; but with potassium, there is always a concurrent reaction with ammonia, catalyzed by the freshly reduced silver. The effectiveness of the reduced silver as a catalyst is greater when potassium is the reducing agent, and also varies with different silver salts, silver cyanide in particular furnishing an active catalyst. The metallic precipitate from most reactions is inert in air, but in the reduction of silver cyanide with potassium a pyrophoric precipitate is obtained. Furthermore, the reduction may extend to the anion of the salt and, in the case of silver thiocyanate, the thiocyanate radical is reduced. The cyanate group, however, is stable in the presence of sodium and potassium in liquid ammonia solution.

The Reduction of Silver Iodide and Silver Chloride

In a previous paper[4] the reduction of silver iodide and silver chloride by sodium was shown to proceed smoothly with the formation of free silver and the corresponding sodium salt. The free silver so formed was non-reactive toward air and did not catalyze the reaction between sodium and ammonia. The ratio between the gram atoms of sodium and gram moles of silver salt reacting (called reaction ratio), was determined accurately and found to be close to 1.00.

Using the same experimental method, with Merck potassium (shown by analysis to be 99.85% potassium) as the reducing agent, higher values for the reaction ratio were obtained and a slight gas formation observed. The method was then modified to permit the collection of the gas. Upon analysis, this proved to be hydrogen. From the hydrogen volume so obtained, the amount of potassium reacting with ammonia was determined and the reaction ratio corrected for this loss of potassium. This was also checked by treating the product of the reaction, after evaporation of the ammonia, with distilled water, which reacted with the potassium amide, and titrating this basic solution, previously boiled, with tenth normal hydrochloric acid. From the acid used, the amount of potassium amide present was calculated, and the reaction ratio corrected for the loss of potassium as determined in this way.

The results of the reduction of silver chloride and silver iodide are given in Table I, in which reaction ratio of column 5 refers to the ratio between gram atoms of potassium and gram moles of silver salt employed; corrected ratios (1) and (2) are the values obtained when the potassium that reacted with ammonia, as determined by the collection of hydrogen and by the amide analysis, respectively, has been subtracted from the total potassium used.

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(1) This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Francis R. Holden in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

(2) Weyl, *Ann. Physik,* **123**, 350 (1864).

(3) Burgess and Rose, THIS JOURNAL, **51**, 2127 (1929).

(4) Burgess and Smoker, *ibid.*, **52**, 3573 (1930).

(5) Burgess and Smoker, *Chem. Rev.*, **8**, 265 (1931).

(6) Kraus, THIS JOURNAL, **30**, 1323 (1908).

TABLE I

REDUCTION OF SILVER CHLORIDE WITH POTASSIUM

Expt.	K, g.	Ag salt, g.	H_2, cc. N. T. P.	Ratio K/AgCl (I)	Corr. ratio (1) K/AgCl (I)	Corr. ratio (2) K/AgCl (I)
22	0.9674	3.3412	[a]	1.06	..	..
112	.4021	1.4358	[a]	1.03	..	1.01
115	.3106	1.1235	2.6	1.01	0.99	1.00
116	.4535	1.5928	5.1	1.04	1.00	1.01
REDUCTION OF SILVER IODIDE						
36	0.4656	2.6785	3.6	1.04	1.02	1.01
41	.3895	2.2636	1.5	1.03	1.02	1.01
45	.3565	2.0614	0.8	1.04	1.03	1.00

[a] Hydrogen not collected.

The reaction ratio is slightly higher than 1.00 as obtained in the sodium reaction but this difference is, without doubt, due to the experimental error in determining the amount of potassium that reacted with the ammonia. Thus, potassium reduces silver chloride and iodide to free silver, with a small amount of concurrent reaction between potassium and ammonia.

The precipitated silver was found to be nonreactive toward air. An analysis of the precipitate from a reaction using silver iodide and potassium, where the precipitate had been washed carefully by a method described in an earlier paper,[3] gave a silver content of 98.5%. This purity is almost the same as found using sodium as the reducing metal and shows that all soluble impurities cannot be removed by washing with liquid ammonia.

Since the reaction with ammonia requires that there always be an excess of reducing metal used, a method was tried by which a large excess of potassium was added to a liquid ammonia solution of the silver salt. Then, after reduction was complete, the excess metal was destroyed by the addition of ammonium bromide. From the gas collected, the excess potassium was calculated. The results are given in Table II.

TABLE II

REDUCTION OF SILVER IODIDE WITH EXCESS POTASSIUM

Expt.	K, g.	AgI, g.	H_2, cc. N. T. P.	Ratio K/AgI	Corr. ratio K/AgI
209	0.3639	1.0428	53.8	2.10	1.01
210	.3344	1.0240	46.4	1.96	1.01

The corrected reaction ratio is 1.01, and shows that this procedure is a satisfactory method for study of these reduction reactions.

The Reduction of Silver Cyanide

The reduction of silver cyanide by sodium was investigated by Kraus and Kurtz,[7] who found that more sodium was necessary for the reaction than would be required for the simple reduction to metallic silver—a reaction ratio of the order of 1.1 being obtained. Preliminary work with sodium, in which the salt was added to the metal solution, gave a high ratio, averaging 1.03. This indicated that the silver might catalyze the reaction between sodium and ammonia. However, the formation of appreciable hydrogen was not detected. But when the silver cyanide was reduced with potassium, the precipitated silver was found to be a catalyst for the reaction between potassium and the solvent, much better than the reduced silver from the iodide or chloride. An accurate determination of the reaction ratio for both sodium and potassium was made by adding an excess of metal to a liquid ammonia solution of the salt and, in the case of sodium, destroying the excess metal with ammonium chloride. Ammonium chloride was not needed with the potassium reaction. The results are shown in Table III.

TABLE III

REDUCTION OF SILVER CYANIDE WITH SODIUM

Expt.	Na (or K), g.	AgCN, g.	H_2, cc. N. T. P.	Ratio Na(K)/AgCN	Corr. ratio Na(K)/AgCN
205	0.2502	0.9780	39.9	1.49	1.00
206	.2432	1.0118	33.1	1.40	1.01
REDUCTION OF SILVER CYANIDE WITH POTASSIUM					
199	0.4708,	0.9967	50.4	1.62	1.01
200	.4420	.9837	41.8	1.54	1.03
203	.3905	1.0185	25.2	1.31	1.02

The corrected reaction ratio approaches 1.00 for sodium, but is slightly higher for potassium. In each case, the reaction parallels that with the other silver salts, except that the precipitated silver is very finely divided and distinctly more reactive. This was especially marked by the fact that the precipitate from experiments numbered 199 and 200 was pyrophoric, bursting into flame when exposed to air. That the activity of the precipitated metal may vary with the salt employed, has not been observed before. In run 203, ammonium chloride was added after the completion of the reaction and this reduced silver was not pyrophoric. Neither was the precipitate pyrophoric in those runs where an excess of silver cyanide was always present or where sodium was the reducing agent.

In some reduction reactions using nickel salts,[8] it has been shown definitely that a high reaction

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(7) Kraus and Kurtz, THIS JOURNAL, 47, 43 (1925).

(8) Eastes, Ph.D. Thesis, University of Cincinnati, 1936.

ratio may be obtained due to hydrogen being adsorbed by the precipitated nickel. It is probable that the slightly higher ratio with potassium in all cases of silver salt reduction is due to a small loss of hydrogen through adsorption by the silver. It is also possible that the reduced silver owes its pyrophoric property to adsorbed hydrogen. In all cases in which the reduced metal was pyrophoric, the formation of hydrogen also occurred. In the work with nickel, it was shown that the addition of ammonium chloride released hydrogen adsorbed by the precipitated nickel. The effect of ammonium chloride in destroying the pyrophoric property of the reduced silver precipitate may be explained in a similar manner. A further study is being made of the nature and properties of pyrophoric precipitates formed by reduction in liquid ammonia.

The Reduction of Silver Thiocyanate and Cyanate

Because of solubility relations, there are relatively few salts that may be used for the reduction reaction in liquid ammonia. Some of the generally soluble salts, in particular the thiocyanates, cyanates and nitrates, have an anion that may not be stable in the presence of such a strong reducing reagent as the alkali metals. Having established a simple reduction in the case of several silver salts, a study was made of the reduction of silver thiocyanate and silver cyanate to determine the stability of these anions. With silver cyanate, excess metal was added to a solution of the salt, while with silver thiocyanate, the salt was added to a solution of the metal. The results are given in Table IV.

TABLE IV

REDUCTION OF SILVER THIOCYANATE WITH SODIUM

Expt.	Na (or K), g.	Ag salt, g.	H_2, cc. N. T. P.	Ratio Na(K)/ Ag salt	Corr. ratio Na(K)/ Ag salt
56	0.2645	1.7698	0.0	1.08	1.08
58	.2148	1.4451	.0	1.07	1.07
75	.4300	2.8657	.0	1.08	1.08
REDUCTION OF SILVER CYANATE WITH SODIUM					
207	0.2491	1.0109	46.3	1.61	0.99
208	.2433	1.0737	38.9	1.48	.99
REDUCTION OF SILVER THIOCYANATE WITH POTASSIUM					
46	0.4637	1.8015	1.4	1.09	1.08
48	.2454	0.9522	1.4	1.09	1.07
71	.3611	1.3745	0.7	1.12	1.11
72	.4605	1.8057	2.3	1.08	1.06
REDUCTION OF SILVER CYANATE WITH POTASSIUM					
201	0.4305	0.9951	48.2	1.66	1.01
202	.4288	1.0023	47.6	1.64	1.00

The average ratio for the reduction of silver thiocyanate is 1.08. This definitely points to another reaction, the most probable being the reduction of the thiocyanate anion. Evidently, the reduction is far from complete. The ratio for the reduction of the silver cyanate approaches 1.00 in each case, thereby proving that silver cyanate is reduced to silver and alkali cyanate, the cyanate radical not being attacked.

To confirm the reduction of the thiocyanate radical, qualitative tests, which were made on the product of the reduction after evaporation of the ammonia, showed the presence of cyanide. Furthermore, potassium was found to react slowly with potassium thiocyanate to form both sulfide and cyanide.

A preliminary study of the reduction of silver nitrate showed that the nitrate radical was readily reduced by both sodium and potassium in liquid ammonia solutions. Silver nitrate diammoniate, $AgNO_3 \cdot 2NH_3$, prepared by evaporating the ammonia from a liquid ammonia solution of silver nitrate, was found to be stable in air at room temperatures, but lost ammonia at 60°. The ratio for the reaction where this salt was added to a solution of the alkali metal, was 5.4 gram atoms of sodium per mole of salt, and 4.6 gram atoms of potassium per mole of salt. The reaction product when sodium was used was black and pyrophoric, and a good catalyst for the reaction between sodium and ammonia, this being the only case where the product of the sodium reduction showed these properties. Some work was done on the reduction of other nitrates with the following results. Using sodium nitrate and sodium, the reaction ratio was 3.5 gram atoms of sodium per mole of salt, and the reaction product was yellow and explosive in air. With potassium nitrate and potassium the ratio was 3.1 and the reaction product was yellow but not explosive. Using ammonium nitrate and potassium, practically no hydrogen was obtained, and the reaction ratio was 3.1 gram atoms of potassium per mole of ammonium nitrate. All of this work shows definitely that the nitrate anion is unstable in the presence of metal solution in liquid ammonia, but further study is necessary to determine the nature of the reduction products.

Summary

Silver salts are reduced by both sodium and potassium in liquid ammonia solution to free silver. This reduced silver may catalyze the reac-

tion between the alkali metal and ammonia. Its efficiency as a catalyst is greater when potassium is the reducing agent and it also varies with the silver salt. With silver thiocyanate, the thiocyanate radical is partially reduced, but with silver cyanate the cyanate group is stable in the presence of either sodium or potassium solutions.

CINCINNATI, OHIO RECEIVED NOVEMBER 14, 1936

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

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solution. V. The Action of Calcium upon Silver Salts

BY WAYLAND M. BURGESS AND FRANCIS R. HOLDEN[1]

Introduction

In a previous paper,[2] the reducing action of the two alkali metals, sodium and potassium, upon a number of silver salts was compared. The reactions were similar, forming free silver and the corresponding alkali metal salt, except that the precipitate from the potassium reactions was reactive in air and a better catalyst for the concurrent reaction between the metal and ammonia. A similar study, in which calcium has been used as the reducing metal, has led to the remarkable results that, with calcium, the reduction reactions are decidedly more vigorous, the precipitated silver is also reactive toward air, and is superior, as a catalyst, to that obtained with potassium. No reference to a previous investigation has been found that would indicate calcium solutions to be a better reducing medium than solutions of the alkali metals.

The Reduction of Silver Iodide and Silver Cyanide

To a solution of silver iodide in liquid ammonia, using an apparatus and procedure described in earlier papers,[2,3] was added an excess of Kahlbaum calcium, found by analysis to be 99.1% calcium. The reaction was rapid and the resulting black precipitate so fine that it settled very slowly. It was such an excellent catalyst for the reaction between calcium and ammonia that the excess metal was converted rapidly into calcium amide and hydrogen. The experimental results showing the amounts of the reacting substances and the volume of hydrogen collected are given in Table I.

TABLE I

REDUCTION OF SILVER IODIDE

Expt.	Ca, g.	Ag salt, g.	H_2, cc. N. T. P.	Ratio 1/2Ca/ AgI(CN)	Corr. ratio 1/2Ca/ AgI(CN)
182	0.2224	1.2903	62.7	2.02	1.00
183	.2709	1.3623	88.3	2.33	0.97
184	.2126	1.1741	62.5	2.12	1.01
REDUCTION OF SILVER CYANIDE					
178	0.2716	1.1993	48.4	1.51	1.03
179	.3254	1.0306	96.6	2.11	0.99
180	.2934	0.7564	100.4	2.59	1.01

Corrected reaction ratio, column 6, has been corrected by subtracting from the total calcium used, the amount of calcium that reacted with ammonia, as determined by the hydrogen collected. This is a true measure of the amount of calcium and silver salt that reacted. This value being 1.0, shows that the silver salt is reduced to free silver. Two concurrent reactions occur as presented by the equations

$$\mathrm{Ca} + 2\mathrm{AgI}\ (\text{or AgCN}) \longrightarrow \mathrm{CaI_2}\ (\text{or } \mathrm{Ca(CN)_2}) + 2\mathrm{Ag}$$

$$\mathrm{Ca} + 2\mathrm{NH_3} \longrightarrow \mathrm{Ca(NH_2)_2} + \mathrm{H_2}$$

In a study of the reaction between silver cyanide and calcium by Kraus and Kurtz,[4] it was postulated that a compound CaAg was formed. The average reaction ratio obtained by them was 2.12, but no attempt was made to determine the amount of hydrogen formed. The present work shows that their high ratio was due to the reaction of calcium and ammonia and that no compound of calcium and silver is prepared in this way.

The precipitated silver from the silver cyanide was pyrophoric and more reactive than that from the silver iodide reaction. In each case, the reduced silver from the calcium reaction was a better catalyst than that obtained by the reduction of the same salt with potassium or sodium. After the completion of one experiment, using calcium and silver cyanide, 0.06 g. of sodium was added to

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(1) This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Francis R. Holden in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

(2) Burgess and Holden, THIS JOURNAL, **59**, 459 (1937).

(3) Burgess and Rose, *ibid.*, **51**, 2127 (1929).

(4) Kraus and Kurtz, *ibid.*, **47**, 43 (1925).

the solution and it was converted to sodium amide in less than fifteen minutes. Silver cyanide reduced by sodium gives silver whose catalytic power is negligible.

The Reduction of Silver Thiocyanate and Silver Cyanate

It has been shown previously[2] that in the reduction of silver thiocyanate to free silver using potassium and sodium, a small amount of the alkali metal was used in the concurrent reduction of the thiocyanate group to sulfide and cyanide. With silver cyanate, the cyanate radical appeared to be stable in the presence of the alkali metal solutions. In view of the more vigorous reduction of the silver iodide and cyanide with calcium, the reaction between silver thiocyanate and calcium offers another opportunity to compare the reducing powers of calcium and the alkali metals. The results obtained by adding an excess of calcium to solutions of sodium thiocyanate are shown in Table II.

TABLE II

REDUCTION OF SILVER THIOCYANATE

Expt.	Ca, g.	AgCNS, g.	H_2, cc. N. T. P.	Ratio 1/2Ca/ AgCNS	Corr. ratio 1/2Ca/ AgCNS
175	0.3949	0.9960	15.2	3.28	3.06
176	.5054	.9979	79.6	4.20	3.01
177	.4705	1.0061	58.4	3.88	3.01

The corrected ratio should be 1.0, if the silver thiocyanate were reduced to silver and no other reaction occurred. The value is close to 3.0, indicating that the reduction of the thiocyanate group to cyanide and sulfide, which requires two additional equivalents of calcium per mole of silver thiocyanate, does occur and goes to completion. The reduction of silver thiocyanate then may be represented by three equations

$$2AgSCN + Ca \longrightarrow 2Ag + Ca(SCN)_2$$
$$Ca(SCN)_2 + Ca \longrightarrow 2CaS + Ca(CN)_2$$
$$Ca + 2NH_3 \longrightarrow Ca(NH_2)_2 + H_2$$

In the reduction of silver cyanate with calcium, it was found that when approximately equivalent amounts of the calcium and silver cyanate were employed, the only reaction to occur was the reduction of the salt to free silver; but with an excess of calcium, a partial reduction of the cyanate radical did occur. These results are shown in Table III, where the first three experiments are with nearly equivalent amounts, and the last three with an appreciable excess of calcium.

TABLE III

REDUCTION OF SILVER CYANATE

Expt.	Ca, g.	AgCNO, g.	H_2, cc. N. T. P.	Ratio 1/2Ca/ AgCNO	Corr. ratio 1/2Ca/ AgCNO
169	0.0213	0.1514	0.5	1.05	1.01
170	.0320	.2275	.5	1.05	1.02
171	.0319	.2148	.8	1.11	1.06
174	.2752	1.0000	62.9	2.06	1.22
166	.3498	1.0020	102.4	2.61	1.24
167	.4367	1.1983	131.7	2.73	1.26

In those experiments where but a very small excess of calcium was used, the corrected ratio shows that little, if any, reduction of the cyanate radical occurred. However, with an excess of calcium, an appreciable reduction of the cyanate group took place. This was also confirmed by the analysis of the products of experiment 174 after evaporation of the ammonia. Strong positive tests for the presence of cyanides were obtained. Thus, we have further evidence that a solution of calcium in liquid ammonia is a stronger reducing agent than solutions of the alkali metals.

Summary

Silver salts are reduced by calcium in liquid ammonia solution to free silver. The reduced silver is pyrophoric and a good catalyst for the reaction between calcium and ammonia. The thiocyanate group of silver thiocyanate is reduced completely to sulfide and cyanide, and the cyanate group of silver cyanate is partially reduced to cyanide when an excess calcium is present.

CINCINNATI, OHIO RECEIVED NOVEMBER 14, 1936

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Infrared Absorption Spectra of Certain Liquid Mixtures

BY WALTER GORDY[1]

Numerous investigations of liquid mixtures[2] have been made recently by means of the Raman spectra. With few exceptions, however, in all of these studies the spectra obtained were the sum of the spectra of the individual components for the lines which were observed. Infrared studies of alcohol–water mixtures[3] and of acetone–water mixtures[4] have revealed bands not characteristic of either of the components. It was suggested that these were associational bands indicating some type of linkage between the two liquids. Associational bands had been reported previously for aqueous solutions[5] of some inorganic acids, hydroxides and salts, and for alcoholic solutions of some hydroxides.[6] More recently[7] a study of alcohol–acetone mixtures has revealed changes in the spectrum of both components indicating association of the two liquids through dipole interaction.

The present work was undertaken as an attempt to determine whether there is association between aniline and certain other liquids, and, if possible, to determine the nature of the linkage. We may anticipate a linkage of aniline with liquids like acetone through the formation of hydrogen bonds, the hydrogen of the NH aniline group forming a bond between the nitrogen of the NH aniline group and the oxygen of the CO acetone group. The hydrogen bond theory[8] has received considerable attention recently.

Experimental

A Hilger infrared spectrometer with a fluorite prism was used throughout the investigation. Cell windows were of fluorite and were sealed with paraffin. The absorbing layer was maintained at a constant thickness of 0.002 cm. by means of mica washers. The chemicals were Baker certified products.

Results

Studies were made of 50% mixtures of aniline with acetone, ethyl acetate, ethyl formate, methyl cyanide, isopropyl ether and carbon tetrachloride. Figure 1 shows the results obtained in the region 2.5 to 3.1 μ. The band appearing at 2.85 μ in pure aniline arises from changes in the vibrational energy of the NH group. For mixtures of aniline with acetone, ethyl acetate, ethyl formate, isopropyl ether and methyl cyanide, this band is shifted to the shorter wave lengths by about 0.05 μ, and its intensity is definitely increased.

These changes are more apparent when the experimental transmission curves for the mixtures are compared with the theoretical transmission curves for a purely mechanical mixture in which no interaction occurs. The theoretical curves are represented by the broken lines in the figure. Here the transmission of the mechanical mixture for a given frequency is represented by

$$T = e^{-f_1 m_1 - f_2 m_2}$$

where f_1 and f_2 are the fractional parts of aniline and the liquid with which it is mixed, respectively, and where m_1 and m_2 are defined by

$$T_1 = e^{-m_1}, \quad T_2 = e^{-m_2}$$

T_1 being the transmission of pure aniline for the given frequency, and T_2 that of the second liquid. It should be remembered that the cell thickness was the same in all cases.

In contrast to the pronounced shifts and changes in intensity observed in the NH band for other mixtures, no measurable changes were observed in the case of mixtures of aniline with carbon tetrachloride, Fig. 1, F.

Figure 2 shows the effects of aniline on the vibrational band of the CO group of acetone, ethyl acetate and ethyl formate. In each of these mixtures the CO band is shifted to the longer wave lengths by approximately 0.05 μ, and in each mixture the intensity of the band is slightly increased. The experimental curves for the mix-

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(1) Now at Mary Hardin-Baylor College.

(2) S. Parthasarathy, *Phil. Mag.* (Suppl.), **17**, 471 (1934); A. Dadieu and K. W. F. Kohlrausch, *Physik. Z.*, **31**, 514 (1930); Whiting and Martin, *Trans. Roy. Soc. Can.*, **25**, 87 (1931); Crigler, THIS JOURNAL, **54**, 4207 (1932).

(3) D. Williams, R. D. Weatherford and E. K. Plyler, *J. Optical Soc. Am.*, **26**, 149 (1936).

(4) D. Williams and E. K. Plyler, *J. Chem. Phys.*, **4**, 154 (1936).

(5) E. K. Plyler and W. Gordy, *ibid.*, **2**, 470 (1934); W. Gordy, *ibid.*, **2**, 62 (1934); E. K. Plyler and E. S. Barr, *ibid.*, **2**, 306 (1934).

(6) E. K. Plyler and F. D. Williams, *ibid.*, **2**, 565 (1934).

(7) W. Gordy, *Phys. Rev.*, **50**, 1151 (1936).

(8) L. Pauling, THIS JOURNAL, **57**, 2680 (1935); *ibid.*, **58**, 94 (1936); L. Onsager, *ibid.*, **58**, 1486 (1936); R. H. Gillette and A. Sherman, *ibid.*, **58**, 1135 (1936); R. H. Gillette and F. Daniels, *ibid.*, **58**, 1139 (1936).

tures should be noted especially in comparison with the theoretical curves for the same mixtures.

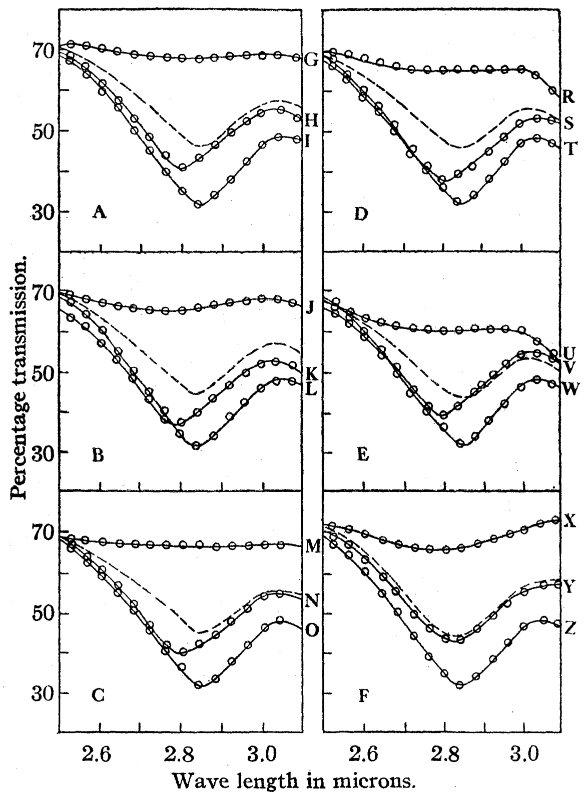

Fig. 1.—Transmission curves in the region 2.5 to 3.1 μ: ----, theoretical for 1:1 mixtures; ——, observed. A, Curve (G) pure isopropyl ether, (H) 1:1 volume mixture with aniline, (I) pure aniline. B, Curve (J) pure acetone, (K) 1:1 volume mixture with aniline, (L) pure aniline. C, Curve (M) pure methyl cyanide, (N) 1:1 volume mixture with aniline, (O) pure aniline. D, Curve (R) pure ethyl formate, (S) 1:1 volume mixture with aniline, (T) pure aniline. E, Curve (U) pure ethyl acetate, (V) 1:1 mixture with aniline, (W) pure aniline. F, Curve (X) pure carbon tetrachloride, (Y) 1:1 mixture with aniline, (Z) pure aniline.

A study was made of aniline bands appearing in the regions of 6.15 μ and 6.65 μ. Transmission curves obtained for these regions are not given. No shifts could be detected in either of the bands for any of the mixtures. Because of overlapping of bands it was not found practicable to study the mixtures in other regions below 8.5 μ.

Discussion

The pronounced changes in the dipole moments of the NH group of aniline and the CO group of acetone, ethyl acetate and ethyl formate, as revealed by changes in the vibrational infrared bands of these groups, in contrast to the approximate constancy of the moments of other groups, indicate association of the liquids through the dipole interaction of these groups. A pos-

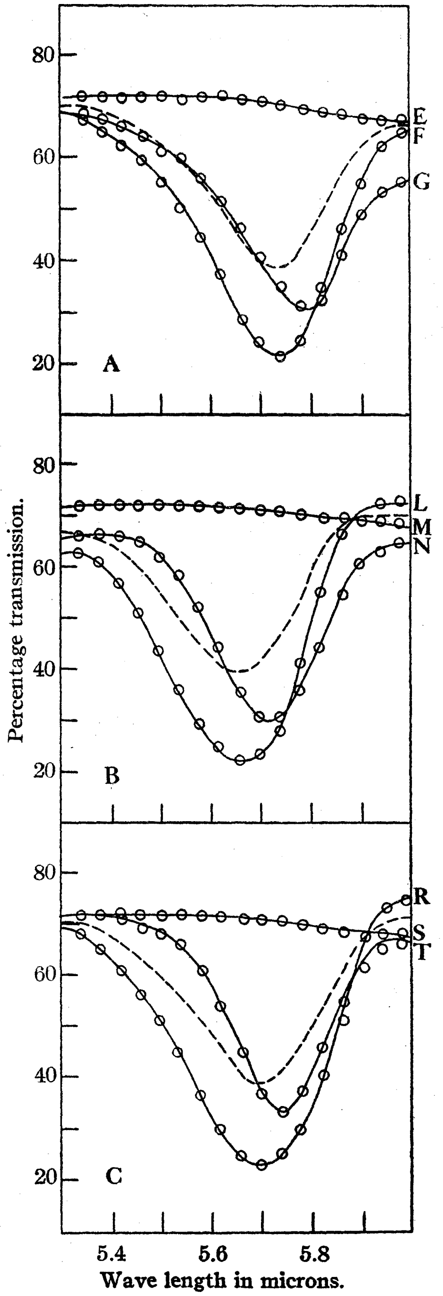

Fig. 2.—Transmission curves in the region 5.3 to 6.0 μ: ----, theoretical for 1:1 mixtures; ——, observed. A, Curve (E) pure aniline, (F) pure acetone, (G) 1:1 volume mixture. B, Curve (L) pure ethyl acetate, (M) pure aniline, (N) 1:1 volume mixture. C, Curve (R) pure ethyl formate, (S) pure aniline, (T) 1:1 volume mixture.

sible explanation of this interaction would be the formation of hydrogen bonds, the hydrogen of the NH aniline group forming a bond between the nitrogen of this group and the oxygen of the CO group. Likewise, the pronounced changes in the NH aniline band in the aniline–isopropyl ether mixtures and the aniline–methyl cyanide mixtures suggest the association of these liquids through the formation of hydrogen bonds. There seems to be no interaction between the NH aniline group and carbon tetrachloride.

The apparent changes in the polarization of molecules in liquid mixtures as determined by dielectric constant measurements are no doubt in many cases due to changes in the electric moments of certain groups resulting from association of the liquids through the interaction of the dipoles of these groups. It should be possible through infra-red absorption measurements to ascertain in many of these mixtures which dipoles undergo pronounced changes and thereby to determine something of the nature of the linkage. The work is being continued on other mixtures in which the formation of hydrogen bonds may be anticipated. Preliminary results,[9] similar to those given above for aniline mixtures, indicate that water and also alcohols associate with certain other liquids through the formation of hydrogen bonds.

The writer wishes to thank Dr. E. K. Plyler for the use of his instrument and Dr. B. G. Carson, of Carson-Newman College, for his helpful discussions.

Summary

In mixtures of aniline with acetone, ethyl acetate, ethyl formate, methyl cyanide and isopropyl ether, the NH vibrational band of aniline is shifted to shorter wave lengths and its intensity is increased. In mixtures of aniline with carbon tetrachloride this band appears to remain constant. Other aniline bands remain approximately constant for all the mixtures. The CO band of acetone, ethyl acetate and ethyl formate is shifted to longer wave lengths, and its intensity increased in mixtures of these liquids with aniline.

It is suggested that the observed changes in the spectrum indicate association of the liquids through dipole interaction. The formation of hydrogen bonds is proposed as a possible interpretation of the results.

BELTON, TEXAS RECEIVED OCTOBER 26, 1936

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[9] Unpublished data obtained by the author.

[CONTRIBUTION NO. 174 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & CO.]

Kinetics of Condensation Polymerization; the Reaction of Ethylene Glycol with Succinic Acid

BY PAUL J. FLORY

Bifunctional condensation polymerizations, such as the formation of polyesters either from hydroxy acids or from glycols and dibasic acids,[1] proceed through the intermolecular reaction of the functional groups attached to bifunctional reactants. The reaction involved is fundamentally no different than the reaction between monofunctional reactants bearing the same functional groups; *e. g.*, in polyester formation the reaction is simply esterification, as Kienle and Hovey[2,3] have shown. Unless the reaction of one functional group of a bifunctional reactant changes the reactivity of the other group, all functional groups may be assumed to be equally reactive. When this is true, the reaction should be of the same kinetic character as the analogous monofunctional reaction. Unpublished experiments carried out in this Laboratory verify this deduction.

Recently Dostal and Raff[4,5] have examined the course of the reaction of ethylene glycol with succinic acid. They combined equimolar quantities either in dioxane solution or in the absence of solvent, and in two sets of experiments the succinic acid was dissolved in a large excess of glycol. The progress of the reaction was followed by titration of the unreacted acid in samples heated for various lengths of time at constant temperatures.

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[1] Carothers, *Chem. Rev.*, **8**, 359 (1931).

[2] Kienle and Hovey, THIS JOURNAL, **52**, 3636 (1930).

[3] Kienle and Hovey, *ibid.*, **51**, 509 (1929).

[4] Dostal and Raff, *Monatsh.*, **68**, 188 (1936).

[5] Dostal and Raff, *ibid.*, **68**, 117 (1936).

Inasmuch as the reaction takes place between two functional groups, Dostal and Raff assume that it is second order. As proof of this they cite the observation that the rate, expressed as the fraction reacting per unit time, increases as the square of the initial concentration when equivalents of the reactants are used. But this observation is actually indicative of a third order mechanism.

In the estimation of approximate activation energies Dostal and Raff use the quantity nE for the critical energy increment in the Arrhenius equation[6] where n is a factor (> 1) depending upon the average degree of polymerization, $\bar{x}$, of the polymer molecules. However, the polymer molecules are not formed through the *simultaneous* formation of several linkages between segments as this expression for activation energy implies, but through the *stepwise* formation of $\bar{x} - 1$ linkages between the $\bar{x}$ segments. The temperature coefficient is simply dependent upon the activation energy E required for one elementary reaction, and so n must equal unity regardless of $\bar{x}$. In view of the confusion in Dostal and Raff's discussion of their results, a re-interpretation seemed desirable.

To this end, for each temperature and concentration at which Dostal and Raff have furnished adequate data, their results have been compared by conventional graphical methods with both bimolecular and trimolecular kinetic equations. When equivalents of the reactants are used the bimolecular equation may be written in the form

$$C_0k_2t = 1/(1 - p) - 1 \qquad (1)$$

where C_0 is the initial concentration in *equivalents* of OH or of COOH groups per liter (Dostal and Raff use *moles* of reactant per liter), k_2 is the velocity constant in liters per equivalent per hour, t is the time in hours, and p is the extent of reaction, *i. e.*, the fraction of the COOH groups which has reacted at time t. For the trimolecular equation

$$2C_0^2k_3t = 1/(1 - p)^2 - 1 \qquad (2)$$

where k_3 is in (liters per equivalent)^2 per hour. When succinic acid was dissolved in a large excess of ethylene glycol, the concentration of the latter remained practically unchanged during the reaction. If the rate is dependent upon the first power of the acid concentration

$$C_gk_2t = -\ln(1 - p) \qquad (3)$$

where C_g is the concentration of glycol. If the rate is proportional to the second power of the acid concentration

$$C_gC_0k_3t = 1/(1 - p) - 1 \qquad (4)$$

where C_0 is the initial concentration of succinic acid.

Although the experimental error in Dostal and Raff's results is rather large, in most cases the reaction was carried far enough to justify a significant choice between the bimolecular (equations (1) or (3)) and trimolecular equations ((2) or (4)). For the reaction of equivalents of acid and glycol, plots of $1/(1 - p)^2$ *vs.* t are invariably more nearly linear than plots of $1/(1 - p)$ *vs.* t. For the reaction of succinic acid dissolved in a large excess of glycol $1/(1 - p)$, but not $\ln(1 - p)$, is approximately linear with t. To illustrate the accordance of the results with equation (2), the bimolecular and trimolecular velocity constants, calculated from equations (1) and (2), respectively, for the reaction of equivalents in the absence of solvent at 123° are given in Table I. It is apparent that k_3 is approximately constant, whereas k_2 decreases as the reaction progresses. Similarly in Table II, k_3 calculated from (4) for the reaction of succinic acid in an excess of glycol is more nearly constant than k_2 calculated from (3).

TABLE I

SECOND AND THIRD ORDER VELOCITY CONSTANTS FOR THE REACTION OF EQUIVALENTS OF ETHYLENE GLYCOL AND SUCCINIC ACID WITHOUT SOLVENT[a]

T = 123°C. C_0 = 13 equiv./liter

t, hours	$1 - p$	$k_2 \times 10^2$, l./equiv./hr.	$k_3 \times 10^2$, l.^{2}/equiv.^{2}/hr.
0	1.000		
.25	0.890	3.8	0.31
.5	.800	3.8	.33
1.0	.682	3.6	.34
2.0	.500	3.8	.44
4.0	.460	2.26	.276
5.0	.420	2.13	.276
6.0	.345	2.31	.365
10.0	.320	1.63	.260
19.0	.250	1.21	.233
24.0	.185	1.41	.347
28.0	.180	1.24	.315

[a] See Table 7 of ref. 4.

Graphically determined values of k_3 at various temperatures and concentrations are given in Table III. Examination of these velocity con-

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[6] Dostal and Raff equate p_2/p_1 (q_2/q_1 in their notation) to the Arrhenius factor $e^{-(nE/R)(1/T_2-1/T_1)}$ where p_1 and p_2 are, respectively, the extents of reaction at temperatures T_1 and T_2 during the times t_1 and t_2 for $t_1 = t_2$. This relationship can only be applied when the extent of reaction is very small. They should have equated t_1/t_2 for $p_1 = p_2$ to the Arrhenius factor.

TABLE II

SECOND AND THIRD ORDER VELOCITY CONSTANTS FOR THE REACTION OF SUCCINIC ACID IN AN EXCESS OF ETHYLENE GLYCOL[a]

$T = 131.5°$ $C_0 = 1$ equiv./liter $C_g = 30$ equiv./liter

t, hours	$1 - p$	$k_2 \times 10^2$, l./equiv./hr.	$k_3 \times 10^2$, l.^{2}/equiv.^{2}/hr.
0	1.000		
.25	0.852	2.14	2.31
.50	.783	1.63	1.85
.75	.735	1.37	1.60
1.00	.679	1.13	1.58
4.25	.380	0.76	1.28
8.00	.214	.64	1.53
14.00	.077	.61	2.86
18.00	.080	.47	2.13
24.00	.070	.37	1.85

[a] See Table II of ref. 5.

TABLE III

VELOCITY CONSTANTS

Source of data Ref.	Table	T., °C.	C_0, equiv./liter[a]	$k_3 \times 10^2$, liter^2/equiv.^{2}/hr.
4	2	150	0.20	~4.5
4	4	150	.50	3.8
4	5	120	1.00	~0.34
4	6	140	1.00	1.65
4	7	123	No solvent[b]	0.30
5	I	131.5	No solvent[b]	.60
5	II	131.5	1.00 acid in glycol[c]	1.43
4	8	140	1.00 acid in glycol[c]	2.70
		1,4-Butylene glycol + succinic acid		
4	9	140	1.00	1.02

[a] Dostal and Raff give concentrations in moles/liter. Unless otherwise stated the solvent was dioxane. [b] Based on the densities of the reactants and assuming no contraction on mixing we take $C_0 = 13$ equiv./liter. [c] Similarly, $C_g = 30$ equiv./liter.

stants obtained over a wide range of concentrations reveals that at a given temperature k_3 is almost independent of the concentration, thus substantiating the choice of kinetic order. It is especially significant that k_3 at 120° at 1.00 equiv./liter is nearly the same as k_3 at 123° in the absence of solvent. It is true, however, that the velocity constants for the reaction of equivalents tend to increase slightly with dilution (*e. g.*, note the 150° k's at $C_0 = 0.20$ and at 0.50), and the velocity constants for the reaction in glycol are greater than those obtained using equivalents. This suggests that a small part of the reaction may be bimolecular. The rates of reaction of 1,4-butylene glycol and of ethylene glycol are comparable at $C_0 = 1.00$ and $T = 140°$.

This analysis shows, therefore, that the reaction of ethylene glycol with succinic acid cannot be bimolecular as Dostal and Raff have supposed; it is approximately trimolecular, the rate being proportional to the first power of the concentration of hydroxyl groups and to the square of the concentration of carboxyl groups.

These results are in harmony with the conclusions reached by Goldschmidt[7,8] from his extensive studies of esterifications, and confirmed by the more recent work of Hinshelwood and coworkers.[9,10] According to these conclusions the esterification reaction requires a hydrion catalyst in addition to a molecule of the alcohol and one of the acid. In the case of esterifications catalyzed by an added acid[7,10] (to which Goldschmidt devoted most of his attention) the hydrion is furnished by this acid. In the "uncatalyzed" reaction the hydrion is furnished by another molecule of the acid undergoing esterification,[8,9] and hence the reaction is trimolecular since two molecules of acid and one of alcohol are required in the formation of the reaction complex. Rolfe and Hinshelwood's observation that the esterification reaction is catalyzed by traces of substances yielding hydrions may explain the irreproducibility in Dostal and Raff's results.

The three energies of activation calculated from the velocity constants in Table III for the polyesterification in the absence of solvent, in dioxane, and in an excess of glycol, respectively, are all within 2 kcal. of 25 kcal. Rolfe and Hinshelwood[9] find a much lower value, 13 kcal., for the reaction of methanol with acetic acid. For the second stage of the reaction of ethylene glycol with phthalic anhydride, *i. e.*, the reaction

$$\text{—O—C}_2\text{H}_4\text{—O—CO—C}_6\text{H}_4\text{—COOH} + \text{HO—C}_2\text{H}_4\text{—O—} \longrightarrow \text{—O—C}_2\text{H}_4\text{—O—CO—C}_6\text{H}_4\text{—CO—O—C}_2\text{H}_4\text{—O—} + \text{H}_2\text{O}$$

Kienle and Hovey[3] have obtained 22.6 kcal. for the activation energy, a value more nearly in agreement with the one for the reaction of glycol with succinic acid.

Polymerization Kinetics and Size Distributions

In a recent paper the author[11] has presented molecular size distribution equations for polymers formed by bifunctional condensations in which it is permissible to assume equal reactivity of all functional groups. By means of these equations the weight-fraction, mole-fraction, or number of any individual molecular species or group of mo-

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(7) Goldschmidt and co-workers, *Z. physik. Chem.*, **60**, 728 (1907); **70**, 627 (1910); **81**, 30 (1913).

(8) Goldschmidt, *Ber.*, **29**, 2208 (1896).

(9) Rolfe and Hinshelwood, *Trans. Faraday Soc.*, **30**, 935 (1934).

(10) Williamson and Hinshelwood, *ibid.*, **30**, 1145 (1934).

(11) Flory, THIS JOURNAL, **58**, 1877 (1936).

lecular species may be calculated. For polymers prepared from equivalents of the reactants the functions are entirely determined by the extent of reaction, p. When an excess of one reactant is used, the distribution functions are expressed as functions of both p and r, where r is the ratio of the initial concentration of the deficient group to the initial concentration of the group present in excess. No application of the equations to the kinetic problem of the relation of the amount of a particular species, or a particular group of species, to time of reaction was discussed. If the kinetic order of the reaction of the functional groups is known, such relationships can be derived by the following procedure. Considering, for example, the number of x-mer molecules N_x

$$\mathrm{d}N_x/\mathrm{d}t = (\partial N_x/\partial p)(\mathrm{d}p/\mathrm{d}t) \qquad (5)$$

since $\mathrm{d}r/\mathrm{d}t = 0$. When $r \neq 1$ the form of the function N_x depends upon whether x is an even or an odd integer; when $r = 1$, $N_x = N_0p^{x-1}(1 - p)^2$ where N_0 is the initial concentration in numbers of molecules. $(\partial N_x/\partial p)$ will be a function of r and p when $r \neq 1$ and of p alone when $r = 1$. From the known kinetics of the process p and $\mathrm{d}p/\mathrm{d}t$ can be expressed as functions of t. Hence, $\mathrm{d}N_x/\mathrm{d}t$ can be expressed in terms of t, and integration will yield N_x as a function of t. In a similar way it is possible to relate the number of molecules within a particular group of sizes $y \leqq x \leqq z$ to time by replacing N_x by $\sum_{x=y}^{x=z} N_x$ in the above equations.

Dostal and Raff have attempted to utilize the size distribution equations in the interpretation of the kinetics of the glycol–succinic acid reaction.[12] Since the size distribution theory is based upon the assumption that the reaction consists of straightforward intermolecular reaction of functional groups, all of equal reactivity, it is obviously useless in an analysis of the kinetics of the reaction of the functional groups. Using the procedure outlined in the preceding paragraph and assuming that the reaction is second order, they have derived an equation for the relation of monomer concentration to time. They attempt to fit this equation in one case (Fig. 9 of ref. 4) to their experimental results which consist of measurements of concentration of COOH groups and not of monomer concentration. There is no foundation for this comparison.

Not having had access to the derivations of the size distribution equations at the time they carried out their work, Dostal and Raff presented the following arguments as proof that these equations are only approximate. First they compared the second order rate of disappearance of monomer given by $\mathrm{d}N_1/\mathrm{d}t = (\partial N_1/\partial p)(\mathrm{d}p/\mathrm{d}t)$ with the rate of disappearance of monomer given by the summation of the second order rates of reaction of monomer with each *other* molecular species, *i. e.*, with the summation $2k\sum_2^\infty N_1N_x$. $\partial N_1/\partial p$ and the concentrations, N_x, of each species were obtained from the distribution equations and substituted in each expression. The two expressions were compared and found to be somewhat different. In the above summation, however, they have omitted the term $2kN_1^2$, which arises from reaction of monomer with monomer. If this term is included, as it obviously should be, the two expressions are found to be identical. In a second similar attempt they have compared the second order rate of change in x-mer concentration given by $\mathrm{d}N_x/\mathrm{d}t = (\partial N_x/\partial p)(\mathrm{d}p/\mathrm{d}t)$ with the rate given by

$$k\sum_{y=1}^{y=x-1} N_yN_{x-y} - 2k\sum_{z\neq x} N_zN_x$$

In the second summation above the term $2kN_x^2$ should not have been excluded, for this term expresses the rate of disappearance of x-mer through reaction with another x-mer. The omission of this term caused Dostal and Raff to obtain nonidentical expressions.

As a result of these errors in setting up the summations, Dostal and Raff were led to the fallacious conclusion that the distribution equations are approximate in character. The distribution equations have been derived without introducing approximations beyond the basic assumption of equal reactivity of all functional groups.

Summary

Using the data of Dostal and Raff, it has been shown that the ethylene glycol–succinic acid polymerization is predominantly a trimolecular process. The rate of the reaction, which is simply an esterification, is proportional to the first power of the concentration of hydroxyl groups and to the square of the carboxyl group concentration. The activation energy for the reaction is about 25 kcal.

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(12) Dostal and Raff at the time they published their paper did not have at their disposal the complete account of the work on size distributions, but only a brief preliminary account included in a paper presented by Carothers [*Trans. Faraday Soc.*, **32**, 39 (1936)] before the Faraday Society, September, 1935.

A number of erroneous conclusions in Dostal and Raff's paper have been pointed out. The relation of the previously published molecular size distribution equations to kinetic problems has been discussed.

WILMINGTON, DEL. RECEIVED DECEMBER 21, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride.[1] XIII. The Alkylation of Benzene with Alcohols

BY JAMES F. McKENNA AND FRANK J. SOWA

Sulfuric acid[2] and aluminum chloride[3,4] have been used to accomplish the condensation of alcohols with benzene.

It was the purpose of this investigation to treat benzene with various alcohols in the presence of boron fluoride. An attempt was also made to determine the course of the reaction by subjecting primary, secondary and tertiary alcohols to the same treatment.

The reaction of alcohols with benzene might proceed by the direct elimination of water from the hydroxyl group of the alcohol and the hydrogen of the aromatic ring (see equation I below) or by first dehydrating the alcohol to an unsaturated compound with subsequent condensation into the aromatic nucleus (equations II and III).

$$CH_3(CH_2)_3\boxed{OH + H}C_6H_5 \longrightarrow CH_3(CH_2)_3C_6H_5 + H_2O \quad \text{I}$$

$$CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH{=}CH_2 + H_2O \quad \text{II}$$

$$CH_3CH_2CH{=}CH_2 + C_6H_6 \longrightarrow CH_3CH_2CH(CH_3)C_6H_5 \quad \text{III}$$

Both *n*-propyl and isopropyl alcohols reacted with benzene to give identical alkylation products, namely: mono-, di-, and tri-isopropylbenzenes. Likewise *n*-butyl and *s*-butyl alcohol both yielded *s*-butylbenzene derivatives. Both isobutyl and *t*-butyl alcohols gave *t*-butylbenzene derivatives.

Since neither *n*-propyl, *n*-butyl nor isobutylbenzenes were isolated from the corresponding primary alcohols, the reaction did not take place to any appreciable extent according to equation (I). The direct elimination of water from the hydroxyl of the alcohol and the hydrogen of the aromatic nucleus therefore does not suggest itself as a plausible mechanism. On the other hand, however, the products of alkylation of benzene with alcohols all indicated that an unsaturated compound was first formed with subsequent condensation into the aromatic nucleus. It is, therefore, proposed that the mechanism of the reaction of benzene with an alcohol is first by dehydration to an unsaturated compound with subsequent condensation of the olefin with benzene according to equations (II) and (III).

Other alcohols besides the *n*-propyl, isopropyl, *n*-butyl, *s*-butyl and *t*-butyl were treated with benzene in the presence of boron fluoride. Cyclohexanol gave mono- and dicyclohexylbenzene; benzyl alcohol yielded mono- and dibenzylbenzene; allyl alcohol gave a small quantity of allylbenzene with a much larger quantity of light brown, high boiling material.

The disubstituted benzenes were the para derivatives with very small quantities of the ortho compounds. The positions were determined by oxidation. Sulfuric acid and boron fluoride both gave the para-substituted dialkylbenzene as the main product with a little ortho and no meta dialkylbenzene. When aluminum chloride is used, as an alkylation agent, in the Friedel–Crafts reaction, however, the main product is most often the meta dialkylbenzene.

The *t*-butyl, benzyl, cyclohexyl, allyl, *s*-butyl and isobutyl alcohols reacted very readily with benzene in the presence of boron fluoride while *n*-propyl and *n*-butyl reacted with more difficulty. Ethylene chlorohydrin reacted only very slightly to give a halogenated compound the structure of which was not determined. Phenol, as would be expected, did not react with benzene. Methyl and ethyl alcohols did not react under the conditions used in this investigation.

Experimental Part

Since the procedure was quite uniform for all of the reactions, only a general one will be described.

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[1] For previous paper see Sowa and Nieuwland, THIS JOURNAL, **58**, 271 (1936).

[2] Meyer and Bernhauer, *Monatsh.*, **53–54**, 721 (1929).

[3] Huston and Hsieh, THIS JOURNAL, **58**, 439 (1936).

[4] Tzukervanik, *J. Gen. Chem.* (*U. S. S. R.*), **5**, 117–120 (1935); *C. A.*, **29**, 4746 (1935).

One mole of either *n*-propyl, isopropyl, *n*-butyl, *s*-butyl, isobutyl, *t*-butyl, benzyl, cyclohexyl or allyl alcohol and one mole of benzene were weighed into a 500-cc. Erlenmeyer flask which was fitted with an inlet tube that extended to within 2 cm. of the bottom and an outlet tube. Boron fluoride was then added, the quantity varied from 20 to 65 g. depending upon the alcohol used. For *t*-butyl alcohol only 20 g. of boron fluoride was necessary and two layers appeared during the addition while *n*-butyl alcohol required 63 g. of boron fluoride and was heated at 60° for a period of nine hours in a closed Pyrex bottle. The most common quantity was 47 g. of boron fluoride; if two layers had not separated after standing overnight it was warmed.

After the reaction mixture was cooled the lower layer was separated and proved to be water, hydroxyfluoboric acid (b. p. 160°) and hydrofluoric acid. The upper layer was washed several times with 75-cc. portions of a 10% solution of sodium hydroxide, then water, dried over calcium chloride, and carefully fractionated through a Widmer column.

TABLE I

ALKYLBENZENES FROM ALCOHOL AND BENZENE

Alcohols used	Nature of alkyl group in benzene	Yield of alkylbenzenes, g. Mono	Di	Poly
n-Propyl	Isopropyl	23.5	14.2	17.6
i-Propyl	Isopropyl	24.4	13.0	10.0
n-Butyl	*s*-Butyl	42.5	21.0	20.0
s-Butyl	*s*-Butyl	35.9	16.9	14.6
i-Butyl	*t*-Butyl	16.2	8.9	21.2
t-Butyl	*t*-Butyl	32.0	21.8	10.1
Cyclohexyl	Cyclohexyl	56.2	27.4	6.4
Benzyl	Benzyl	23.2	15.1	34.0 (Above 250° at 15 mm.)
Allyl	Allyl	8.7	31.1 (Above 165°)	

TABLE II

PHYSICAL PROPERTIES OF ALKYLBENZENES

Alkylbenzene	B. p., °C.	n_D^{25}	Sp. gr., 25°
n-Propylbenzene	157	1.4925	0.8656
i-Propylbenzene	151	1.4885	.8581
Diisopropylbenzene	204	1.4892	.8550
s-Butylbenzene	171	1.4880	.8577
s-Dibutylbenzene	237	1.4880	.8548
t-Butylbenzene	167	1.4905	.8623
t-Dibutylbenzene	M. p. 77°		
Cyclohexylbenzene	235	1.5190	.9338
Dicyclohexylbenzene	M. p. 100–102°		
Benzylbenzene	261	1.5697	1.0043
Dibenzylbenzene	M. p. 84–85°		
Allylbenzene	156–159	1.5042	0.8812

The results of several runs are given in Table I and the physical properties are tabulated in Table II.

Oxidation of Dialkylbenzenes.—In order to determine the position of the alkyl group in the dialkylbenzenes, oxidation of the side chains to well-known benzene derivatives was used. The phthalic acids or their methyl esters differ widely in melting points.

Several methods of oxidation of diisopropylbenzene were tried but the only successful method was by the use of dilute nitric acid.

Two grams of diisopropylbenzene was refluxed with 300 cc. of 25% nitric acid for twenty hours. An 85% yield of a phthalic acid was obtained. After recrystallization from hot water and drying the acid sublimed without melting above 300°, indicating terephthalic acid. This acid was heated with absolute methyl alcohol in the presence of hydrogen chloride. On cooling a mass of white crystals separated in the form of thin plates. The crystals melted at 140°, which checks with the dimethyl ester of terephthalic acid. No metaphthalic ester could be detected. A separate sample of the acid was tested for ortho phthalic acid by conversion to fluorescein. The test indicated the presence of the ortho isomer but in very small quantity.

The structure of *p*-*s*-dibutylbenzene and of *p*-*t*-dibutylbenzene was best determined by oxidation with chromic acid in acetic acid solution.

The structures of most of the other para dialkylbenzenes have been determined previously and the physical properties of the compounds in this investigation checked well with them.

Summary

Benzene has been alkylated by normal and iso as well as secondary and tertiary alcohols in the presence of boron fluoride.

Normal and secondary alcohols give identical products; iso- and *t*-alcohols also give identical alkylation products.

A mechanism for the alkylation of benzene with alcohols has been proposed.

Boron fluoride, in general, gives different dialkylbenzenes than aluminum chloride, as the main product, when used as an alkylating agent.

The ease of reaction has been found to be dependent upon the ease of dehydration of the alcohol.

NOTRE DAME, INDIANA RECEIVED DECEMBER 19, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 577]

The Kinetics of the Thermal Isomerization of Cinnamic Acid Catalyzed by Iodine

BY ROSCOE G. DICKINSON AND H. LOTZKAR

It is well known that *cis–trans* isomerizations at ethylenic linkages can be catalyzed by various substances including iodine,[1] but the kinetics of this iodine catalysis have received comparatively little attention. The kinetics of the iodine-sensitized photochemical conversion of *cis*- into *trans*-cinnamic acid have been examined in benzene solution by Berthoud and Urech,[2] whose results are interpretable in terms of an iodine-atom catalysis. The results of the present thermal experiments likewise carried out in benzene solution indicate a close relation between the photochemical and thermal reactions.

Materials.—*cis*-Cinnamic acid was prepared by the reduction of phenylpropiolic acid by hydrogen using colloidal palladium as a catalyst; the method was essentially that of Paal and Hartmann.[3] The phenylpropiolic acid was prepared through the bromination of ethyl cinnamate and subsequent treatment with alcoholic potash; the procedures were those described in "Organic Syntheses,"[4] and the yields reported there were obtained. The colloidal palladium used in the reduction of the phenylpropiolic acid was prepared by the reduction of palladous chloride by hydrogen in aqueous solution in the presence of sodium protalbinate.[5] To effect the reduction of phenylpropiolic acid, the colloidal palladium protected by protalbinate was added to sodium phenylpropionate in somewhat alkaline solution. The solution was placed in a 200-cc. flask connected with a gas buret; the flask was evacuated and one mol of hydrogen added for each mol of phenylpropionate taken. After reduction, the solution was acidified, whereupon the *cis*-cinnamic acid separated as an oil. This was extracted with ether, treated with sodium carbonate and reprecipitated as oil with acid. In one preparation the oil was converted to the aniline salt and crystallized from a ligroin and benzene mixture.[6] The *cis*-cinnamic acid was then liberated with hydrochloric acid and recrystallized from water. In a second preparation, the formation of an aniline salt was omitted. The oil was frozen repeatedly using solid carbon dioxide, whereupon the oil crystallized. It was then twice recrystallized from water. The melting point of the first preparation was from 48 to 53°; that of the second was from 58 to 65°. Both preparations were evidently mixtures of *cis*-cinnamic acids for both gave the same equivalent conductance, 73.3, in 0.003 M solution at 25°. Values obtained by other observers are: Bjerrum, 72.5;[7] Vaidya, 74;[8] Olson and Hudson, 72.8.[9]

The *trans*-cinnamic acid was an Eastman product recrystallized from hot water.

The water was commercial distilled water redistilled from alkaline permanganate. The specific conductance of the water at 25° was 1.0×10^{-6} mho cm.$^{-1}$.

Thiophene-free benzene was used.

The iodine was a Merck product.

Analytical Method.—Conductance measurements were employed to determine the fraction of *cis*-cinnamic acid in mixtures of *cis*-cinnamic acid with *trans*-cinnamic acid. For this purpose the specific conductances of a series of known mixtures of the two acids were measured in 0.003 volume molal solution at 25°. The results are given in Table I.

TABLE I

SPECIFIC CONDUCTANCES AT 25° OF MIXTURES OF *cis*- AND *trans*-CINNAMIC ACIDS AT 0.003 M

% *cis*-acid	100	90.0	80.0	70.0	60.0	50.0	40.0	30.0	20.0	10.0	0
$\bar{L} \times 10^4$	2.200	2.108	2.025	1.934	1.838	1.743	1.641	1.537	1.421	1.307	1.188

These conductivities were plotted on a large scale and a smooth curve drawn. The cell constant used in these measurements was obtained from measurements on 0.001 N potassium chloride solution using Shedlovsky's value, 146.93, for the equivalent conductance at 25°.[10]

Experimental Procedure.—Stock solutions with appropriate known concentrations of *cis*-cinnamic acid and of iodine in benzene were prepared. In carrying out an experiment, 5.00 cc. of cinnamic acid solution and 5.00 cc. of iodine solution were pipetted into a 15-cc. ampoule and sealed off with the exclusion of light. The ampoule was then placed for a measured period of time in a light-tight chamber surrounded by the vapor of a boiling liquid (water was used in some experiments and methylcellosolve in others); in any one experiment the temperature range was less than 0.1°. The ampoule was then removed, cooled with water, opened and the contents transferred to a flask. The benzene and iodine were then pumped off at room temperature. These manipulations were carried out in red light or in the dark. The colorless residue of cinnamic acids (whose weight was presumed to be that of the *cis*-cinnamic acid taken) was dissolved in such a quantity of water as to give a 0.00300 M solution. The conductivity of the solution was then measured in a thermostat at 25°.

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[1] See, *e. g.*, C. Liebermann, *Ber.*, **23**, 512 (1890).

[2] A. Berthoud and Ch. Urech, *J. chim. phys.*, **27**, 291 (1930).

[3] C. Paal and W. Hartmann, *Ber.*, **42**, 3930 (1909).

[4] "Organic Syntheses," Vol. XII, John Wiley and Sons, Inc., New York, 1932, pp. 36, 60.

[5] C. Paal and C. Amberger, *Ber.*, **37**, 132 (1904).

[6] C. Liebermann, *ibid.*, **23**, 2515 (1890).

[7] N. Bjerrum, *ibid.*, **43**, 571 (1910).

[8] B. K. Vaidya, *Proc. Roy. Soc.* (London), **A129**, 291 (1930).

[9] A. R. Olson and F. L. Hudson, THIS JOURNAL, **55**, 1410 (1933).

[10] T. Shedlovsky, THIS JOURNAL, **54**, 1424 (1932).

TABLE II

SPECIFIC RATE CONSTANTS FOR THE CONVERSION OF *cis*- INTO *trans*-CINNAMIC ACID

No.	Initial concn. of *cis*-cinnamic acid, mole/liter	Concn. of iodine, mole/liter	Temp., °C.	Heating time, hours	Specif. cond. at 0.003 *M*, mho cm.$^{-1}$ × 10^4	*trans*-Cinnamic acid formed, %	k_T moles$^{-1/2}$ × liters$^{1/2}$ × hrs.$^{-1}$	$k_{122.5°}$ moles$^{-1/2}$ × liters$^{1/2}$ × hrs.$^{-1}$
1	0.03	0.0015	99.4	24	2.088	13.0	0.150	
2	.03	.0015	99.4	50	1.974	25.7	.153	
3	.03	.0015	99.4	100	1.808	43.3	.146	
4	.09	.024	99.4	24	1.836	40.4	.139	
5	.03	.0015	122.2	10	1.913	32.3	1.007	1.033
6	.03	.0015	122.2	35	1.484	74.8	1.017	1.042
7	.03	.0015	122.8	19	1.700	54.1	1.057	1.033
8	.03	.003	122.9	15	1.676	56.5	1.012	0.983
9	.03	.006	122.2	11	1.675	56.6	0.978	1.001
10	.03	.012	122.9	5	1.801	44.0	1.057	1.024
11	.03	.012	122.9	8	1.642	59.8	1.037	1.007
12	.03	.024	122.6	6.5	1.602	63.8	1.011	1.003
13	.09	.0015	122.7	8	1.964	26.7	1.002	0.988
14	.09	.006	122.8	10	1.716	52.5	0.960	.935
15	.09	.024	122.4	6.5	1.639	60.1	.910	.920

When a blank experiment was made by evaporating 20 cc. of benzene alone and any residue dissolved in 100 cc. of water, the specific conductance of the water changed from 1.0 × 10^{-6} to 1.3 × 10^{-6} mho cm.$^{-1}$. The analytical conductivity measurements were corrected for this change. Blank experiments in which iodine was heated with benzene in the absence of cinnamic acid, gave no more conductivity change than the benzene above. A blank experiment was made in which a benzene solution 0.03 *M* (volume molal) in cinnamic acid and 0.0015 *M* in iodine was prepared and immediately analyzed without heating; the conductivity of the resulting 0.003 *M* aqueous solution was 0.0002191 (corrected) in satisfactory agreement with the value 0.0002200 expected for pure *cis*-cinnamic acid.

A series of experiments was made starting with *trans*-cinnamic acid. In one of these a benzene solution 0.03 *M* in *trans*-cinnamic acid and 0.0015 *M* in iodine was heated for ninety-one hours at 99.4°. In no case did the measured conductivity differ significantly from that expected for pure *trans*-cinnamic acid; accordingly, in interpreting measurements of the *cis–trans* conversion, reverse reaction has been regarded as negligible.

Experimental Results.—The kinetic measurements are given in Table II. The initial concentrations given are in moles per 1000 cc. at 22°; the *k*'s given in the table are calculated in terms of these concentrations from the equation:

$$k = \frac{1}{t(\mathrm{I_2})^{1/2}} \ln \frac{(C)_0}{(C)}$$

where (C) is the concentration of *cis*-cinnamic acid. This equation arises from integration of the equation $-\mathrm{d}(C)/\mathrm{d}t = k(C)\ (\mathrm{I_2})^{1/2}$. Since the temperatures obtained with methylcellosolve varied somewhat from one experiment to another, the rate constants measured using it have been reduced to the temperature 122.5° by means of the Arrhenius equation.

In the tabulated experiments, the initial concentration of *cis*-cinnamic acid has been varied three-fold, and the iodine concentration sixteen-fold; at the upper temperature the ratio of *trans*- to *cis*-acid present at the end of an experiment varied from 0.37 in expt. 13 to 3.0 in expt. 6. In all of these experiments except those (nos. 4, 14, 15) where the concentrations of both acid and iodine were comparatively high, constancy of *k* within probable experimental error was found. The somewhat lower values of *k* found at the highest concentrations are possibly attributable to addition of I_2 to the double bond of cinnamic acid. Dissociation constants of the order of 0.5 mole/liter for the assumed di-iodo compounds would suffice to account for this apparent trend.

The mean values of the constants obtained with the lower cinnamic acid concentration (0.03 *M*) are 0.150 at 99.4° and 1.013 at 122.5° the units being moles, liters at 22° and hours. When the units used are moles, cc. at the temperature of the reaction and seconds, these constants become 1.39 × 10^{-3} at 99.4°, and 9.59 × 10^{-3} mole$^{-1/2}$ cc.$^{1/2}$ sec.$^{-1}$ at 122.5°. Between these temperatures, the ten-degree multiplication of the constant is accordingly 2.28.

Discussion.—The fact that the thermal reaction is of one-half order with respect to I_2 suggests that the catalytic agent is atomic iodine just as in the photochemical reaction.[2] A reaction scheme which then leads to the type of rate expression found experimentally is the following

$$\begin{array}{rll} I_2 \rightleftharpoons 2I & (1) \text{ and } (1') \\ I + C \rightleftharpoons AI & (2) \text{ and } (2') \\ AI \rightleftharpoons BI & (3) \text{ and } (3') \\ BI \rightleftharpoons T + I & (4) \text{ and } (4') \end{array}$$

Here C and T represent *cis*- and *trans*-cinnamic acid; AI and BI represent the molecules resulting from the addition of an iodine atom to these two respective acids. The reversal of all steps has been included in order explicitly to avoid possible conflict with the principle of microscopic reversibility. In order for a conversion of one isomer into the other to occur, in effect a rotation about the ethylenic bond is necessary; this presumably occurs after the addition of the iodine atom. Furthermore, an odd number of inversions of carbon tetrahedra is necessary if a tetrahedral character be attributed to both the ethylenic carbons in the iodine atom addition compound. Whether such inversions occur in the acts of addition and removal of the iodine atom as well as in reactions (3) and (3′), or whether inversion occurs only in reactions (3) and (3′), cannot be decided from the present experiments; nor can these possibilities be distinguished from the case where tetrahedral character is not ascribed to both carbons of the compounds AI and BI so that inversion becomes unnecessary. This latter case is covered in the rate expression given below if k_3 be placed equal to $k_{3'}$ and made very large. The usual treatment of the reaction scheme given above leads, on the assumption that I, AI and BI remain at low concentration, to the following rate expression

$$-\frac{d(C)}{dt} = \sqrt{\frac{k_1}{k_{1'}}(I_2)}\;\frac{k_2k_3k_4\,(C) - k_{2'}k_{3'}k_{4'}\,(T)}{k_{2'}k_{3'} + k_{2'}k_4 + k_3k_4}$$

Evidently k_1/k_1' is the dissociation constant of iodine into atoms, and $k_2k_3k_4/k_{2'}k_{3'}k_{4'}$ is the equilibrium constant for the transformation of *cis*- into *trans*-cinnamic acid. Since, in experiments starting with *trans*-cinnamic acid, any isomerization was small, the term in (T) may, for purposes of the experiments of Table II, be dropped. This leaves a rate expression of the form of that found empirically, *viz.*, $-d(C)/dt = k(C)(I_2)^{1/2}$ with $k = \sqrt{\frac{k_1}{k_{1'}}}\,\frac{k_2k_3k_4}{k_{2'}k_{3'} + k_{2'}k_4 + k_3k_4}$.

The local rate (thin layer) of the photochemical conversion is reported to be given by the[2] expression $-d(C)/dt = k_{Ph}I_0^{1/2}(I_2)^{1/2}(C)$ where I_0 is the radiation incident per unit area per unit time. Assuming the photochemical reaction to proceed by the same mechanism as the thermal except for replacement of step (1) by $I_2 + h\nu \longrightarrow 2I$, it is readily seen that $k/k_{Ph} = \sqrt{k_1/\alpha}$, where α is the molal absorption coefficient of iodine for the wave length used. On the assumption that α varies relatively little with temperature it follows that at a given temperature $d \ln k/dT - d \ln k_{Ph}/dT = {}^1/_2 d \ln k_1/dT$. The multiplication of the photochemical rate between 25 and 35° at constant concentrations and intensity is given as 1.3. From this the over-all activation energy of the photochemical reaction may be calculated from the Arrhenius equation $d \ln k_{Ph}/dT = Q_{Ph}/RT^2$ treating Q_{Ph} as constant with temperature; the value obtained is 4800 cal. Similarly, for the thermal reaction the Q obtained is 24,200 cal. Hence, for reaction (1), $Q_1 = 2(24{,}200 - 4800) = 38{,}800$ cal. There is evidence[11] that reaction (1′) goes at every kinetic theory collision and accordingly requires no activation energy. If this be the case, Q_1 should equal ΔH for the dissociation of molecular iodine in benzene solution. The value of ΔH for the dissociation of gaseous iodine at 18° obtained with the aid of spectroscopic data[12] is 36,270 cal./mole. Since heats of solution of gases in non-polar solvents often amount to several thousand calories[13] extremely close agreement between the dissociation energies in solution and gas is not to be expected. The reasonably close agreement found in the present case lends independent support to the supposition that the iodine catalysis is brought about by iodine atoms.

Summary

Rates of isomerization of *cis*- into *trans*-cinnamic acid as catalyzed by iodine have been measured in benzene solution at 99.4 and 122.5°. The rates have been found to be substantially of first order with respect to *cis*-cinnamic acid and half-order with respect to iodine. This result has been interpreted as indicating an iodine atom catalysis such as has been supposed to occur in the

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[11] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 547 (1936).

[12] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, 1936, p. 189.

[13] For example, from the tabulations of Bichowsky and Rossini,[12] the following values for the heat content increase, ΔH, per mole on vaporization from various solutions at 18° may be obtained: I_2 from C_6H_6, 8910 cal.; Br_2 from CCl_4, 7150; Cl_2 from CCl_4, 4500; HCl from CCl_4, 3620; O_2 from H_2O, 3850; H_2 from H_2O, 1420. The value of ΔH for the vaporization of atomic iodine from benzene solution calculated from that for molecular iodine together with Q_1 and ΔH for the gaseous dissociation, is 3200 calories per atomic weight.

photochemical iodine-sensitized reaction. Comparison of the temperature coefficients of the thermal and photochemical reactions leads to a calculation of the energy of dissociation of iodine into atoms in benzene solution and gives further evidence in favor of the supposition of an iodine atom catalysis.

PASADENA, CALIF. RECEIVED DECEMBER 21, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

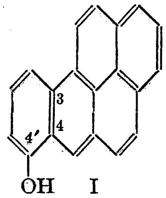
Hydroxy Derivatives of 3,4-Benzpyrene[1] and 1,2-Benzanthracene

BY L. F. FIESER, E. B. HERSHBERG,[2] L. LONG, JR., AND M. S. NEWMAN[3]

The study of hydroxy derivatives of carcinogenically active hydrocarbons was undertaken partly because it is of interest to determine the influence of hydroxyl and modified hydroxyl substituents on the cancer-producing properties of the hydrocarbons, and partly in the hope of broadening the field of biological experimentation. If suitable functional groups can be introduced without complete loss of carcinogenic activity, it should be possible to attach to the carcinogens side chains of such a character as to vary the solubility relations in different directions. Hydroxy compounds would be of further interest, as Cook and his associates[4] have observed, because polynuclear aromatic compounds arising in the body as products of the metabolism of steroids might be expected to appear in an hydroxylated form comparable with oestrone and equilenin.

From the information now available, the most potent of the known carcinogenic hydrocarbons can be classified as either 10-alkyl-1,2-benzanthracenes or as compounds containing the 1,2-benzanthracene ring system with a carbon substituent in the alternate meso position 9.[5] Methylcholanthrene, cholanthrene, 9,10-dimethyl-1,2-benzanthracene and 10-methyl-1,2-benzanthracene are the most powerful agents of the first type, while 3,4-benzpyrene is the most active representative of the second type of hydrocarbon. On the basis of this provisional classification, a systematic investigation has been undertaken to determine the influence of hydroxyl, amino and other groups at various positions on the carcinogenic properties of these hydrocarbons. The results presented in this paper are incidental observations which constitute a start in the direction indicated.

The synthesis of 4′-hydroxy-3,4-benzpyrene (I) was reported in a preliminary communication,[6]



I

and further details of the preparation of the compound and of various derivatives are given in this paper. The hydroxyl group of this compound occupies position 5 in the 1,2-benzanthracene ring system present in the molecule. Dr. M. J. Shear injected the crystalline hydroxy compound into mice and obtained no tumors at the site of injection after sixteen months. Negative results were obtained also with 4′-ketotetrahydro-3,4-benzpyrene, from which I is prepared by dehydrogenation. The action of 4′-methoxy-3,4-benzpyrene suggested that it may prove to be weakly carcinogenic, although it is too early to make a definite decision. Experiments with the acetate, benzoate, *p*-aminobenzoate, and carboxymethyl derivative are in progress.

Although 1,2-benzanthracene itself is almost completely devoid of cancer-producing properties,[7] the fact that some of the simple alkyl derivatives of the hydrocarbon are potent carcinogenic agents suggested the idea of testing samples of the 3-hydroxy and 3-methoxy compounds which were available from an earlier research

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(1) Revised numbering system, see Note 7, THIS JOURNAL, **58**, 2377 (1936).

(2) Lilly Research Fellow.

(3) Now at The Ohio State University.

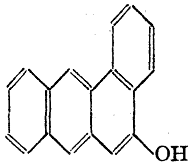
(4) Cook, Haslewood, Hewett, Hieger, Kennaway and Mayneord, "Reports of the II International Congress of Scientific and Social Campaign against Cancer," **1**, 1 (1936); *Am. J. Cancer*, **29**, 219 (1937).

(5) Fieser and Hershberg, THIS JOURNAL, **59**, 394 (1937); L. F. Fieser, M. Fieser, Hershberg, Newman, Seligman and Shear, *Am. J. Cancer*, **29**, 260 (1937).

(6) Fieser, Hershberg and Newman, THIS JOURNAL, **57**, 1509 (1935).

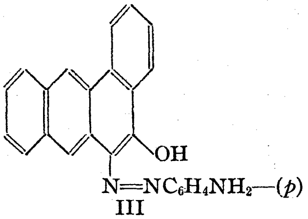
(7) Barry, Cook, Haslewood, Hewett, Hieger and Kennaway, *Proc. Roy. Soc.* (London), **B117**, 318 (1935).

of one of us with Dietz.[8] As the preliminary tests of Dr. Shear gave interesting results, the experiments were repeated with fresh samples of the compounds and a few additional derivatives were prepared. 3-Hydroxy-1,2-benzanthracene (II) gave entirely negative results in one experiment with eleven mice, but in another experiment tumors were obtained at the site of injection in two of ten mice after eight months. These mice were males and the tumors were in immediate contact with injected material still present. 3-Methoxy-1,2-benzanthracene has given tumors at the site of injection in several animals and the tumors have been found to be transplantable. Both the hydroxy compound and the ether appear to have carcinogenic properties, although the action in each case is slow and irregular. No tumors have been obtained as yet with the benzoate (eight months) or stearate (six months). It is of interest that 9-methoxy-1,2,5,6-dibenzanthracene has been found to possess carcinogenic activity.[7]



II

In view of the discovery by Yoshida[9] that *o*-aminoazotoluene has carcinogenic properties, it seemed of interest to investigate the *p*-aminobenzeneazo derivative of 3-hydroxy-1,2-benzanthracene, III. A product presumably containing this compound was obtained in an amorphous condition by the alkaline hydrolysis of the crystalline acetate resulting from the coupling of the hydroxy compound with diazotized N-acetyl-*p*-phenylenediamine. Nitrogen-containing compounds are of further interest because of carcinogenic properties of 2-(*p*-aminostyryl)-6-(*p*-acetylaminobenzoylamino) - quinoline methoacetate,[10] because of the biological changes produced by 3,4,5,6-dibenzcarbazole,[4] and because of the indications that aromatic amines may be responsible for cases of bladder-cancer among workers engaged in the manufacture of dyestuff intermediates.[4] For this reason, 3-hydroxy-1,2-benzanthracene was converted into 3-amino- and 3-methylamino-1,2-benzanthracene by the Bucherer reaction, and tests with the compounds are now in progress.



III

Experimental Part[11]

4′ - Keto - 1′,2′,3′,4′ - tetrahydrobenzpyrene.—Sannié and Poremski[12] have pointed out that in preparing this ketone by the method very briefly described by Fieser and Fieser[13] it is advisable to employ carefully purified γ-3-pyrenylbutyric acid and to remove the excess thionyl chloride as completely as possible. These specifications were included in the original directions but they are properly emphasized. Although the acid should be of good quality (from xylene[13]), purification through the ester[14] is not necessary. The importance of carefully eliminating the excess thionyl chloride was established by adding some of the reagent to one of two portions of a satisfactory sample of the acid chloride in carbon bisulfide solution. On subsequently adding stannic chloride, a copious black precipitate separated at once and the final product was of an inferior grade. In the parallel test there was very little immediate precipitation of black material and the bright purple-red complex slowly formed. It is important to avoid overheating the acid chloride during the preparation. The reaction of the acid with thionyl chloride can be hastened safely by warming the mixture in a water-bath maintained at 40°, and in removing the ether at reduced pressure this bath temperature should not be exceeded or the material may be spoiled. The first evaporation leaves a yellow oil which largely solidifies on adding fresh ether. On removing the solvent again and distributing the product over the walls of the flask, the acid chloride forms a hard, nearly colorless cake streaked in places with yellow. After evaporating fresh portions of ether and of carbon bisulfide, the yellow streaks disappear and the product is obtained as a light gray solid, m. p. 76–77°. The cyclization can be conducted satisfactorily at 25°, followed by refluxing. On using four times the amount of stannic chloride specified, the yield of ketone dropped to 46–49%. Water may be used at the end of the reaction in place of ice and, as the red complex is unusually stable, steaming should be continued for some time. The crude ketone, which has been obtained repeatedly in a good condition in 80–85% yield, can be purified by distillation in vacuum or, very satisfactorily, by crystallization from dioxane. The purest sample obtained melted at 174–174.5°.

4′-Hydroxy-3,4-benzpyrene.—The best results were obtained by heating a mixture of 2 g. of the pure ketone (from dioxane) and 0.24 g. of sulfur at 210–215° for seventy to

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[8] Fieser and Dietz, This Journal, **51**, 3141 (1929).

[9] See Cook, *et al.*,[4] for references.

[10] Browning, J. B. Cohen, Cooper, Ellingworth and Gulbransen, *Proc. Roy. Soc.* (London), **B113**, 300 (1933).

[11] The melting points are corrected except as noted. Analyses by Mrs. G. M. Wellwood.

[12] Sannié and Poremski, *Bull. soc. chim.*, [5], **3**, 1139 (1936).

[13] Fieser and Fieser, This Journal, **57**, 782 (1935).

[14] Fieser, Fieser and Hershberg, *ibid.*, **58**, 1463 (1936).

eighty minutes, distilling the product at reduced pressure, and crystallizing the distillate from xylene; yield, 0.6 g. (30%), m. p. 216–218°. Recrystallized from xylene, the substance formed yellow needles with a bronze luster, m. p. 218–219°.

The **acetate**, prepared by refluxing the hydroxy compound with acetic anhydride and sodium acetate for two hours, was crystallized from acetic acid and then from absolute alcohol. It formed small, yellow needles, m. p. 194–195°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 84.75; H, 4.77.

The **benzoate** was obtained with the use of benzoyl chloride and pyridine (two hours on the steam bath) and crystallized from benzene–absolute alcohol; flat yellow needles, m. p. 191–192°.

Anal. Calcd. for $C_{27}H_{16}O_2$: C, 87.07; H, 4.33. Found: C, 86.74; H, 4.71.

For the preparation of the **methyl ether,** 0.3 g. of the hydroxy compound was dissolved in a solution of 1 g. of potassium hydroxide in 20 cc. of 50% alcohol and treated in the cold with 2 cc. of dimethyl sulfate. After adding more alkali and more reagent, the ether (0.28 g.) was precipitated with water and crystallized from benzene–absolute alcohol. It formed pale yellow-orange, flat prisms, m. p. 183–184°.

Anal. Calcd. for $C_{21}H_{14}O$: C, 89.33; H, 5.00. Found: C, 89.38; H, 5.14.

The **carboxymethyl derivative** was obtained by the action of excess chloroacetic acid on hydroxybenzpyrene dissolved in aqueous potassium hydroxide and dioxane under varying conditions, but the yield at best was only about 30%. The crude material obtained on acidification of the solution was dried and dissolved in acetone. Benzene was added, and after removing most of the acetone by distillation the product separated as rosets of fine, yellow needles, m. p. 243–244°.

Anal. Calcd. for $C_{21}H_{14}O_3$: C, 80.23; H, 4.52. Found: C, 79.97; H, 4.12.

The ***p*-nitrobenzoate,** prepared as above, crystallized from benzene–ligroin as shiny brown needles, m. p. 252–253°.

Anal. Calcd. for $C_{27}H_{15}O_4N$: C, 77.68; H, 3.62. Found: C, 77.85; H, 3.57.

The ***p*-aminobenzoate** was obtained in excellent yield by the hydrogenation of the nitro compound in warm dioxane solution using Adams catalyst. When the color of the solution had changed from yellow-orange to pale yellow-green, the filtered solution was diluted with water and the crystalline precipitate was crystallized from dioxane–alcohol. The amine formed pale yellow needles, m. p. 268–269°.

3-Methoxy-1,2-benzanthracene.—The reduction of crude 3-methoxy-1,2-benz-10-anthrone with aluminum amalgam and alcoholic ammonia was reported by Fieser and Dietz[8] to give somewhat irregular results, the yields varying from 25 to 65%. The reaction seems to be particularly sensitive to the nature of the aluminum metal, and in the present work we had little success using the aluminum turnings on hand and only slightly better results with aluminum foil. A more reliable method of reduction was found in the use of activated zinc dust, sodium hydroxide, and toluene.[15]

Fifty grams of zinc dust was shaken with a solution of 2.5 g. of copper sulfate in 100 cc. of water and the supernatant liquor was decanted. The crude anthrone from 20 g. of 4-methoxy-1-naphthylphenylmethane-2′-carboxylic acid was added, together with 800 cc. of 1 *N* sodium hydroxide solution and 300 cc. of toluene. In some experiments the anthrone was employed in the moist condition originally obtained;[8] in others the moist material was suspended in water, the acid present was neutralized with ammonia and the product was collected and dried before use in the reduction. The reaction mixture was boiled under reflux for eight hours, during which time the aqueous layer changed in color from dark brown to red to red-brown while the toluene layer remained yellow. The liquor was filtered hot into a separatory funnel and a separation was made at once. The toluene solution deposited nearly colorless needles of 3-methoxy-1,2-benzanthracene, and additional material was obtained from the mother liquor, which was combined with benzene extracts of the aqueous layer and of the zinc residue. The total yield of material of average melting point 160–161°, uncorr., was 11 g. (63%). Repeated crystallization from glacial acetic acid gave colorless needles, m. p. 167–168°.

3-Hydroxy-1,2-benzanthracene Benzoate.—The hydroxy compound, prepared according to Fieser and Dietz,[8] was heated with benzoyl chloride in pyridine solution at the boiling point for a few minutes. On dilution with water and cooling, the benzoate separated as long, pale yellow needles. Recrystallization from alcohol gave long, colorless needles, m. p. 174–174.5°; it is readily soluble in dioxane, moderately so in benzene, sparingly soluble in alcohol.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.24; H, 4.63. Found: C, 85.82; H, 4.94.

3-Hydroxy-1,2-benzanthracene Stearate.—A solution of 0.5 g. of hydroxybenzanthracene and 0.8 g. of stearyl chloride (from the acid with thionyl chloride, b. p. 179–182° at 4 mm.) in 5 cc. of dry pyridine was heated for two hours on the steam bath and cooled. On adding 5–6 drops of 0.5 *N* potassium hydroxide solution, an amorphous white precipitate separated. Washed with 50% pyridine solution and dried, the crude material (1.2 g.) melted at 72–78°. After digestion with small portions of methanol, in which the substance is only moderately soluble, the bulk of the material was crystallized from this solvent and obtained as small, colorless needles, m. p. 87–89° (0.5 g.). The melting point was not changed on further crystallization.

Anal. Calcd. for $C_{36}H_{46}O_2$: C, 84.65; H, 9.09. Found: C, 84.33; H, 8.84.

Carboxymethyl Derivative of 3-Hydroxy-1,2-benzanthracene.—A mixture of 0.5 g. of hydroxybenzanthracene, 1.8 cc. of 33% aqueous sodium hydroxide solution, 2 cc. of dioxane, and 2 cc. of water was warmed until solution was complete, cooled (two layers), treated with 1.3 cc. of 50% aqueous chloroacetic acid solution and heated at 100° for three hours. The solution was diluted with water,

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(15) Martin, THIS JOURNAL, 58, 1438 (1936).

made acid to Congo red paper and the product was extracted with ether, taken into dilute soda solution and precipitated by acidification. Crystallization from toluene, using decolorizing carbon, gave colorless needles, m. p. 216–217°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.20; H, 4.99. Found: C, 78.93; H, 4.89.

4 - *p* - Acetaminobenzeneazo - 3 - hydroxy - 1,2 - benzanthracene.—A solution of 0.615 g. of N-acetyl-*p*-phenylenediamine, prepared according to Nietzki,[16] and purified by vacuum distillation and crystallization from water, in 5.1 cc. of glacial acetic acid was treated with 0.4 cc. of concentrated sulfuric acid, which precipitated the sulfate, cooled to 17°, and treated slowly with 1.2 cc. of ice-cold isopropyl nitrite. To the resulting red solution 20 cc. of absolute ether was added, which precipitated the diazonium salt as an oil. After decanting the cloudy liquid, the oil was dissolved in 5 cc. of glacial acetic acid and on adding ether the diazonium salt was precipitated in a crystalline, somewhat pink, condition. The salt, suspended in 10 cc. of glacial acetic acid (in which the crystalline material is sparingly soluble) was added to a mechanically stirred solution of 0.5 g. of 3-hydroxy-1,2-benzanthracene in 47 cc. of glacial acetic acid at 17°. A deep red suspension of the azo compound was soon obtained, and after stirring for one and one-half hours the mixture was diluted with 50 cc. of water, stirred for fifteen minutes, and the product was collected. The crude azo compound melted at 275–279°, uncorr.; yield 0.72 g. (95%). Crystallized from a large volume of benzene, the substance formed small, lustrous red needles, m. p. 278–279°, uncorr. It is sparingly soluble in all ordinary solvents.

Anal. Calcd. for $C_{26}H_{19}O_2N_3$: C, 77.00; H, 4.73. Found: C, 77.10; H, 4.50.

4 - *p* - Aminobenzeneazo - 3 - hydroxy - 1,2 - benzanthracene.—The hydrolysis of the acetate presented difficulties and the amine was not obtained in a completely pure condition. Of a number of methods of hydrolysis with acids and alkalies investigated, the following was the most satisfactory. The acetate (1.4 g.) was refluxed with 420 cc. of a 10% solution of potassium hydroxide in absolute alcohol for nineteen hours and the hot solution was filtered from a small amount of brown residue and diluted with 300 cc. of hot water. The material which separated on cooling was washed with 50% alcohol, and then washed with water until free from alkali. The amine was obtained in this way as an amorphous, deep brownish-purple powder melting at 211–213°, uncorr.; yield 0.54 g. (43%). It is practically insoluble in all solvents tried except pyridine, and it did not crystallize from the solvent. Analyses of the amorphous material indicated the presence of impurities (Calcd. for $C_{24}H_{17}ON_3$: C, 79.3; H, 4.7; N, 11.6. Found: C, 80.5; H, 5.2; N, 9.2).

3-Amino-1,2-benzanthracene.—A mixture of 1 g. of 3-hydroxy-1,2-benzanthracene, 5 g. of sodium bisulfite in 10 cc. of water, 10 cc. of concentrated ammonia solution, and 5 cc. of dioxane was heated in a sealed tube at 180–190° for ten hours. After dilution with water, the crystalline product was collected, dried and crystallized from absolute alcohol; yield 0.65 g. (65%), m. p. 209–210°. After further crystallizations the substance formed fan-shaped clusters of yellow needles, m. p. 211.5–212.5°. The amine is very slightly soluble in hot, dilute hydrochloric acid.

Anal. Calcd. for $C_{18}H_{13}N$: N, 5.76. Found: N, 5.86.

3 - Methylamino - 1,2 - benzanthracene.—This derivative was prepared exactly as described above except that 33% aqueous methylamine solution was substituted for the ammonia solution; the yield of pure material was 38%. Crystallized from alcohol, in which it is much more soluble than the primary amine, the compound formed rosets of short, flat, yellow needles, m. p. 115.5–116.5°.

Anal. Calcd. for $C_{19}H_{15}N$: N, 5.45. Found: N, 5.73.

Summary

The preparation of various functional derivatives of 4′-hydroxy-3,4-benzpyrene and of 3-hydroxy-1,2-benzanthracene is described and it is reported that 3-hydroxy- and 3-methoxy-1,2-benzanthracene have weak carcinogenic properties.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED JANUARY 16, 1937

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[16] Nietzki, *Ber.*, **17**, 343 (1884).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND CORNELL UNIVERSITY]

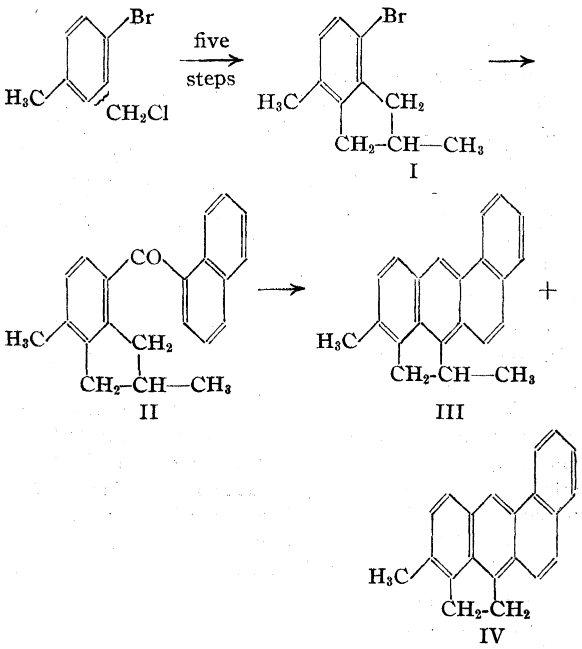
Carcinogenic Hydrocarbons. I. 15,20-Dimethylcholanthrene[1]

BY W. F. BRUCE WITH L. F. FIESER

In order to study the effect of optical isomerism on carcinogenic potency, hydrocarbons related to the active carcinogenic agents cholanthrene and methylcholanthrene and possessing also a center of asymmetry are being synthesized and tested biologically. The synthesis of 16,20-dimethylcholanthrene was accomplished by Fieser and Seligman,[2] but Shear has found[3] that the average time of the appearance of tumors following the injection of the hydrocarbon into mice is about seven and one-half months, as compared with about two and one-half months for 20-methylcholanthrene. In view of this surprising increase in the time required for the appearance of tumors as a result of the added methyl group at C_{16}, it seemed desirable to investigate the effect of a methyl group in the alternate position of the five-membered ring, and consequently the synthesis of 15,20-dimethylcholanthrene (III) was undertaken.

The synthesis was accomplished using the general method of the methylcholanthrene synthesis[4] and utilizing in the initial steps a process which has been described by Bachmann, Cook, Hewett and Iball[5] in a paper published since the completion of this part of the present work. The mixture of isomers resulting from the chloromethylation of *p*-bromotoluene[4] was condensed with ethyl methylmalonate and the product was hydrolyzed, decarboxylated, and cyclized to a mixture of dimethylbromohydrindones. On Clemmensen reduction the mixture yielded pure 2,7-dimethyl-4-bromohydrindene (I). From the Grignard reagent of I with α-naphthoyl chloride, the ketone II was obtained, and on pyrolysis it yielded a mixture from which the desired hydrocarbon (III) was separated in an apparently pure condition.

After three crystallizations from propyl alcohol the substance melted at 134–136°, a value which was not changed by another crystallization.



This material was secured in very small yield; the principal part of the hydrocarbon from the pyrolysis was methylcholanthrene (IV), the formation of which involved loss of the methyl group on the carbon adjacent to the point of ring closure. This series of reactions is unsuitable for the production in quantity of either methylcholanthrene or 15,20-dimethylcholanthrene.

Experimental Part[6]

2,7-Dimethyl-4-bromohydrindone.—Since our preparation of 2,7-dimethyl-4-bromohydrindone was anticipated by Bachmann, Cook, Hewett and Iball, the steps leading to this substance may be summarized briefly. From a mixture of 2- and 3-chloromethyl-4-bromotoluenes[3] a mixture of the corresponding diethyl methylbromobenzylmethylmalonic esters was prepared (yield 83.6%, b. p. 168–170° at 1.6 mm.) and from it by hydrolysis with potassium hydroxide and acidification the malonic acid mixture (yield 95%, m. p. 163–165°, dec.) was obtained. The malonic acid mixture was decarboxylated at 170°, giving the propionic acid mixture (yield 98%, m. p. 74–76°) which was converted through the acid chloride to a mixture of hydrindones boiling at 121–142° at 1.5 mm. (yield 95%). The mixture (d^{30}_{30} 1.27) on distillation was separated rather sharply into two fractions of which one, comprising 20% of the total, boiled at 125° (1.5 mm.) and the other at 145° (1.5 mm.). The lower boiling portion ap-

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[1] Originating as a summer problem (1935) in the Converse Memorial Laboratory, Harvard University, this work was completed at the Baker Laboratory, Cornell University, and has been under the supervision of Professor Fieser.—W. F. B.

(2) Fieser and Seligman, THIS JOURNAL, **57**, 1377 (1935).

(3) Shear, *Am. J. Cancer*, **28**, 334 (1936).

(4) Fieser and Seligman, THIS JOURNAL, **57**, 942 (1935).

(5) Bachmann, Cook, Hewett and Iball, *J. Chem. Soc.*, 60 (1936).

(6) Semimicroanalyses by E. L. Martin and R. G. Larsen; microanalyses by W. F. Bruce.

pears to be the 2,7-dimethyl-4-bromohydrindone (b. p. 115–117° at 0.15 mm.) of Bachmann, Cook, Hewett and Iball, for like theirs it failed to crystallize. The higher boiling portion solidified and after four crystallizations from petroleum ether the 2,4-dimethyl-7-bromohydrindone melted at 81°.

Anal. Calcd. for $C_{11}H_{11}OBr$: C, 55.23; H, 4.64. Found: C, 55.25; H, 4.76.

2,7-Dimethyl-4-bromohydrindene (I).—The mixture of hydrindones was reduced by the Clemmensen method according to the technique of Fieser and Seligman. From 27 g. of hydrindone mixture 22 g. (87%) of 2,7-dimethyl-4-bromohydrindene was obtained. The substance is a colorless mobile liquid with a kerosene-like odor boiling at 104–106° (2.5 mm.).

Anal. Calcd. for $C_{11}H_{13}Br$: C, 58.66; H, 5.82. Found: C, 58.77; H, 6.14.

4-(α-Naphthoyl)-2,7-dimethylhydrindene (II).—The ketone was prepared by allowing the Grignard reagent prepared from the hydrindene to react with α-naphthoyl chloride according to the procedure of Fieser and Seligman.[8] It was advantageous in the preparation of the Grignard reagent to add a few drops of ethyl bromide to the ethereal solution of the hydrindene rather than to the initial portion only. From 10 g. of the hydrindene 4.3 g. (48%) of a light yellow oil boiling at 200° (1 mm.) was secured. Upon four crystallizations from petroleum ether rosets melting at 80–81° separated.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.9; H, 6.7. Found: C, 87.4; H, 6.6.

In addition 3.0 g. of a hydrocarbon, presumably **2,4-dimethylhydrindene,** boiling at 105–106° (25 mm.) was isolated.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.64. Found: C, 89.8; H, 9.7.

15,20-Dimethylcholanthrene.—For pyrolysis 2.5 g. of the ketone was heated for one-half hour at 405–410°. A light yellow fraction boiling at 200–210° (0.5 mm.) and weighing 0.6 g. (23.5%) was secured. This material readily formed a dark purple picrate which after three crystallizations from benzene melted at 179–180° and weighed 0.4 g. This material was washed with warm dilute ammonia to remove picric acid, leaving 0.3 g. of a pale yellow solid. This was crystallized from benzene and petroleum ether and yielded 0.25 g. of yellow solid melting at 163–165°. This was dissolved in anhydrous benzene and passed twice through a tower containing activated alumina, by which a considerable amount of dark colored material was removed. The product melting at 169–171° was sublimed in a small molecular still, by which more dark colored material was left behind, and was again crystallized from benzene and petroleum ether. The solution deposited 0.06 g. of light yellow silky needles melting sharply at 174–175° (177.5–178.5°, corr.). A mixed melting point with methylcholanthrene (177–178°, corr.) showed no depression.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Calcd. for $C_{21}H_{16}$: C, 93.98; H, 6.02. Found: C, 93.9; H, 6.4.

From the Elbs condensation there was obtained, in addition to this fraction, 1.1 g. of a dark red very viscous oil boiling from 240–250° at 0.5 mm. This portion formed very little picrate and failed to crystallize from petroleum ether.

From the mother liquor after the first crystallization of the picrate a second crop of crystals (0.15 g.) was secured. After three recrystallizations, the substance melted fairly sharply at 173–174°. The picric acid was removed by warm alcoholic ammonia, and the residue was purified by microsublimation. The product melted at 120–122°, and the mixed melting point with methylcholanthrene was 117–120°. After three crystallizations from propyl alcohol, the substance melted at 134–136°, mixed melting point with methylcholanthrene 120–126°. Purification involved a large loss of material since the product was more soluble than the impurity, methylcholanthrene.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.58; H, 6.43. Found: C, 93.49; H, 6.42.

Summary

The synthesis of 15,20-dimethylcholanthrene has been accomplished by the method of Fieser and Seligman, but the yield is very low because the pyrolysis results in loss of the methyl group adjacent to the point of ring closure, giving 20-methylcholanthrene as the chief product, and 15,20-dimethylcholanthrene in smaller amount.

RECEIVED JANUARY 20, 1937

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, COLLEGE OF ENGINEERING, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Infrared Absorption of Liquid and Gaseous 1,4-Dioxane between 1.4 and 14.0 μ

BY D. S. MCKINNEY, C. E. LEBERKNIGHT AND J. C. WARNER

The infrared absorption of liquid and gaseous dioxane has been investigated between 1.4 and 14.0 μ using a rock salt spectrometer. The region from 2.27 to 3.72 μ also has been studied using a prism-grating spectrometer. The 1,4-dioxane was purified by refluxing over metallic sodium using a 24-inch (61-cm.) fractionating column packed with short pieces of glass tubing. The fraction used boiled at 99.3–99.4° at 738 mm.

The rock salt spectrometer consists of an equilateral prism 8.5 cm. on an edge so arranged as to pass the energy through the prism twice, thus securing a high resolving power without the necessity of using extremely narrow slits. Effective slit widths for various spectral regions are as follows

Region (μ)	4	7	12	14
Effective slit (μ)	0.01	0.01	0.02	0.06

Effective slit widths, in wave numbers, are given in Figs. 1 and 2. The existing data on the dispersion of rock salt were not considered accurate enough for the calibration of the instrument. It was therefore necessary to select suitable materials for calibration. The following established bands and lines were used:

Sodium D lines (mean)	0.5893 μ		
Benzene band at	2.464 μ		
Q branches of ethylene bands at	5.292 μ	6.925 μ	10.53 μ

The data of Cross[1] were used to interpolate between the calibration points. It has been found possible to resolve the above ethylene bands practically as well as done by Levin and Meyer[2] using grating instruments. The spectrometer is enclosed in a steel case. The thermocouple, its leads and the galvanometer, are also shielded in steel pipe. The shielding and spectrometer are grounded. The steel spectrometer case is covered with a Masonite case to prevent local changes in temperature.

The grating instrument consisted of an echelette grating with a resolving power of 15,000 in the first order and a small angle rock salt prism which was used to eliminate lower order energy. The energy was measured by means of compensating single-junction vacuum thermocouples connected to a Leeds and Northrup high voltage sensitivity galvanometer. The deflections of this galvanometer were amplified by means of an optical relay. The calculations of Firestone[3] concerning the relation between the speed of response and resistance of the thermocouple were confirmed. Due to external disturbances, extreme care had to be taken to ensure stability in the receiving system. The unique features of the rock salt spectrometer and the receiving system will be published elsewhere. This report will describe in detail the means of ensuring stability even when operating near the limit of sensitivity fixed by the Brownian motion of the first galvanometer.

A survey of the spectrum of liquid dioxane from 1.4 to 14.0 μ (Fig. 1, top) using a 0.2-mm. cell showed four regions of intense absorption at 880, 1100, 1350 and 2800 cm.$^{-1}$, and regions of moderate absorption at 1720, 1950, 3550 and 4200 cm.$^{-1}$. The regions of intense absorption were first studied using 0.02-mm. cells (marked C, Fig. 1). The correct thickness in these cells was obtained by rolling lead sheet to the desired thickness and cutting washers from the lead ribbon which were used as spacers between the rock salt windows. In the regions around 880, 1100, 1350 and 2800 cm.$^{-1}$ absorption was still intense with the 0.02-mm. cell. These regions were therefore investigated using a cell in which the windows were pressed together with only a capillary film of dioxane between (curves marked B, Fig. 1). With this cell there was still almost complete absorption in the regions of 880 and 1100 cm.$^{-1}$. These regions were finally studied using a cell made up of carefully polished flat rock salt windows, held together by small spring clips (curves marked A, Fig. 1). Since the wave number resolving power of the prism instrument is rather poor at shorter wave lengths than 4 μ, the regions of wave number 2800 cm.$^{-1}$ and greater were studied in detail on the prism grating spectrometer. The effective slit widths, in wave numbers, for the various spectral regions, are marked in Figs. 1 and 2. The regions 880,

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[1] Cross, *Rev. Sci. Instruments*, **4**, 197 (1933).

[2] Levin and Meyer, *J. Optical Soc. Am. and Rev. Sci. Inst.*, **16**, 137 (1928).

[3] Firestone, *Rev. Sci. Instruments*, **1**, 630 (1930).

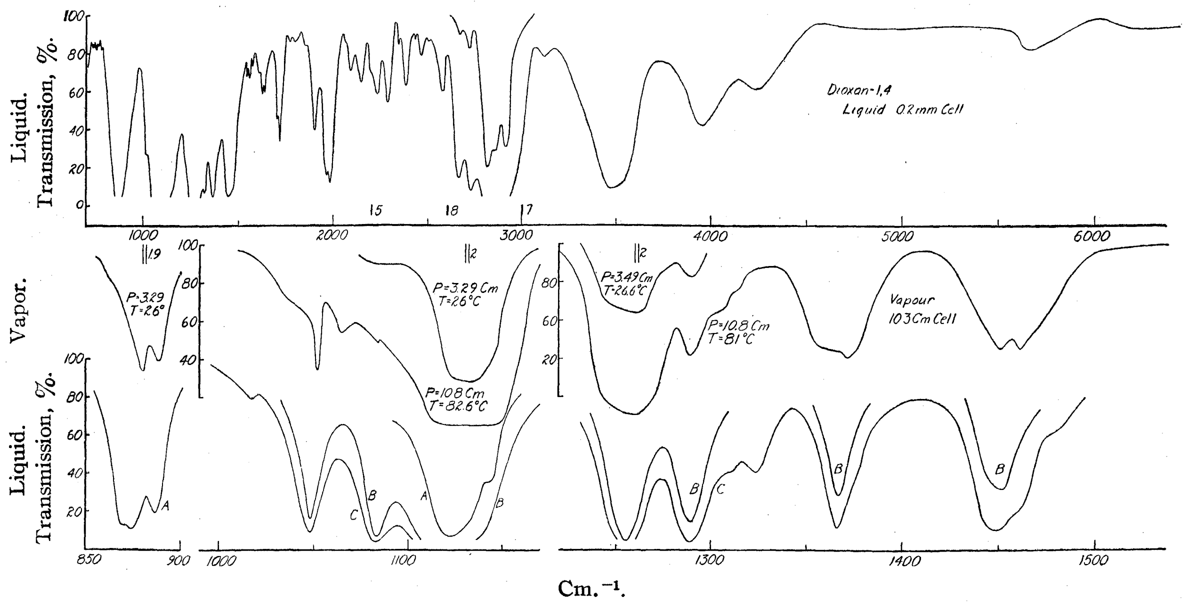

Fig. 1.—Liquid: A, very thin cell; B, moderately thin cell; C, 0.02-mm. cell.

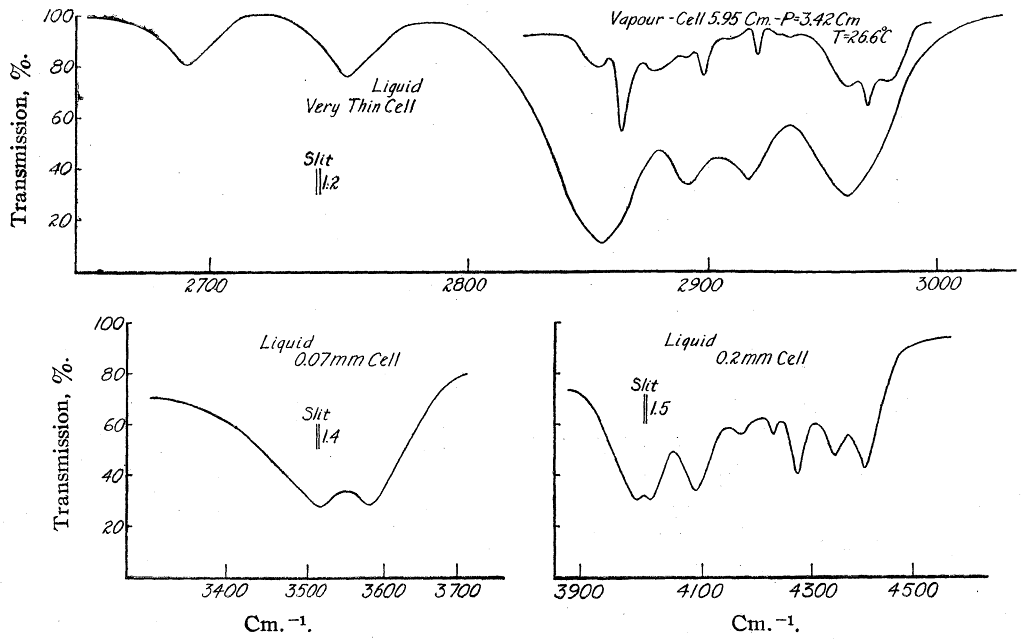

Fig. 2.

1100 and 1350 cm.$^{-1}$, using thin liquid cells, are shown to a larger scale in the lower part of Fig. 1. Each region is seen to be composed of a number of bands (3 in 880, 5 in 1100 and at least 5 in 1350 cm.$^{-1}$ region).

The absorption of gaseous dioxane was next investigated in a 10.3-cm. cell with rock salt windows containing dioxane vapor. To guard against the condensation of liquid dioxane on the windows, the cell was filled with a mixture of 20% dry air and 80% dry air saturated with dioxane vapor. With this concentration of dioxane only the more intense bands were observed. To secure higher concentration without increasing the cell length, a cell was made with a small bulb sealed to one side containing liquid dioxane. This cell and side bulb were heated electrically, always maintaining the cell at a higher temperature than the side bulb. The temperature of the bulb determines the vapor pressure of dioxane in the cell, while the higher temperature of the cell prevents condensation on the windows. The dioxane pressures (in cm.) and the cell temperatures are recorded on Figs. 1 and 2.

Comparison with the vapor shows that the bands are not markedly different from the liquid, the shift in the location of the bands is toward higher frequencies in the vapor and is not constant for the various components. The vapor band at 1050 cm.$^{-1}$ shows evidence of rotation (envelope of vibration–rotation band).

The regions at 2880, 3550 and 4200, cm.$^{-1}$ were studied with the grating spectrometer (Fig. 2). At 2880, 6 bands were found in the liquid. Of these the four most intense were studied in the vapor, where again the envelope of the vibration–rotation bands is clear. The shifts for these bands are again unequal:

$\bar{\nu}$ in Liquid	Shift in vapor
2854.9	+8.5
2891.0	+7.1
2916.6	+4.4
2960.8	+8.9

Furthermore, the breadths of the two bands 2855 and 2961 are not the same, the latter being 24 wave numbers (which is the same as that at 1050 cm.$^{-1}$) and the former 34 wave numbers. The bands at 3550 and 4200 wave numbers were studied only in the liquid state. That at 3550 was resolved into a doublet. The 4200 bands show a more complicated structure. Table I shows the positions of the bands studied in detail on the prism spectrometer and comparison with the Raman spectra.[4–6] Table II shows the positions of the bands studied on the grating, and comparison with the Raman Spectra.[4–6] In all 55 bands were found. The comparison with

TABLE I

FREQUENCIES OBSERVED IN THE INFRARED ABSORPTION OF LIQUID AND GASEOUS DIOXANE. SOME FREQUENCIES FROM RAMAN SPECTRUM GIVEN FOR COMPARISON. (WAVE NUMBERS CM.$^{-1}$) PRISM SPECTROMETER

Infrared frequencies			Raman frequencies		
Liquid	Gas		K. and S.[a]	W. and S.[b]	V.[c]
			430 (3)		
			487 (4)		
870 (vs)			833 (9)	836	837
874 (vs)	880				
887 (vs)	889				
1017 (s)			1014 (6)	1017	
1048 (s)	1052				
	1065				
1083 (s)	1084		1107 (3)		
1122 (vs)	1133		1123 (3)	1117	1115
1142 (s)			1215 (4)		
	(mean)	(peak)			
1256 (vs)	1255	1261			
1289 (vs)	1290		1303 (7)		
1322 (s)			1333 (0)	1306	
	(mean)	(peak)			
1367 (s)	1367	1371			
1452 (s)	1451		1442 (6)	1450	1442
	1461		1460 (2)		
1543 (w)					
1558 (w)					
1574 (w)					
1610 (w)					
1624 (w)					
1636 (w)					
1703 (m)					
1717 (m)					
1771 (w)					
1797 (w)					
1855 (w)					
1899 (m)					
1964 (m)					
1982 (m)					
2087 (w)					
2143 (w)					
2234 (w)					
2286 (w)					
2344 (w)					
2380 (w)					
2433 (w)					
2502 (w)					
2575 (w)					

(vs) very strong
(s) strong
(m) moderate
(w) weak

[a] K. and S., Kohlrausch and Stockmair, *Z. physik. Chem.*, **B31**, 382 (1936).

[b] W. and S., Wolkenstein and Syrkin, *J. Chem. Phys.*, **3**, 594 (1935).

[c] V., Villars, THIS JOURNAL, **52**, 4612 (1930).

TABLE II

FREQUENCIES OBSERVED IN THE INFRARED ABSORPTION OF LIQUID AND GASEOUS DIOXANE. SOME FREQUENCIES FROM RAMAN SPECTRUM GIVEN FOR COMPARISON. (WAVE NUMBERS CM.$^{-1}$) PRISM-GRATING SPECTROMETER

Infrared frequencies		Raman frequencies		
Liquid	Gas	K. and S.	W. and S.	V.
2690 (m)		2663 (0)		
2752 (m)		2720 (3)	2720	
2855 (vs)	2863	2854 (8b)	2852	2864
2891 (vs)	2898	2895 (4)		
2917 (vs)	2921			
2961 (vs)	2970	2963 (9b)	2967	2971
3118 (w)		3040 (0)		
3513 (s)				
3582 (s)				
3988 (m)				
4011 (m)				
4085 (m)				
4164 (m)				
4224 (m)				
4272 (m)				
4343 (m)				
4402 (m)				
5652 (w)				
6200 (w)				

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(4) Villars, THIS JOURNAL, **52**, 4612 (1930).

(5) Wolkenstein and Syrkin, *J. Chem. Phys.*, **3**, 594 (1935).

(6) Kohlrausch and Stockmair, *Z. physik. Chem.*, **B31**, 382 (1936).

Raman spectra shows good agreement, especially with the results of Kohlrausch and Stockmair. The superior resolving power of the prism spectrometer used in this work is illustrated by comparison with the work of Gordy[7] on dioxane–water mixtures using a fluorite prism spectrometer. In the region 5.9 to $6.5\,\mu$ (1695 to 1538 cm.$^{-1}$) Gordy used too thin a cell (0.02 mm.) to detect the six weak bands found by us. In the region from 4.4 to $5.2\,\mu$ (2273 to 1923 cm.$^{-1}$) Gordy finds one band at $5.05\,\mu$ (1980 cm.$^{-1}$). Our instrument resolves this band into two at 1964 and 1982 cm.$^{-1}$. The single band found by Gordy at $3.38\,\mu$ (2959 cm.$^{-1}$) was resolved by our prism instrument into three bands as shown in the curve inserted in Fig. 1 (top). Subsequent examination on the grating spectrometer showed four bands at 2855, 2891, 2917 and 2961 cm.$^{-1}$ (Fig. 1, bottom).

The authors acknowledge with thanks a grant-in-aid from the National Research Council to one of us (J. C. W.), which made possible the construction of the rock salt prism spectrometer.

Summary

The infrared absorption of liquid and gaseous 1,4-dioxane has been investigated between 1.4 and 14.0 μ using a rock salt spectrometer of unusually high resolving power. The region from 2.27 to 3.72 μ has also been investigated using a prism - grating spectrometer. The absorption in the gas is not much different than that observed in the liquid. In passing from the liquid to the gas there is a slight shift to higher frequencies: For example, the liquid bands in the 3.45 μ region are shifted 4 to 9 wave numbers, and the vapor band shape is characteristic of the envelope of vibration–rotation lines.

PITTSBURGH, PENNA. RECEIVED JANUARY 15, 1937

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[7] Gordy, *J. Chem. Phys.*, **4**, 769 (1936).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions of Electrolytes as a Function of the Concentration. V. Sodium Chloride

BY GRINNELL JONES AND SCHUYLER M. CHRISTIAN

This paper gives data on the viscosity of aqueous solutions of sodium chloride at both 25 and 0° from 0.002 up to 2 *N*. The earlier papers[1] of this series should be consulted for a discussion of the historical background and theoretical interest of the problem.

The best measurements at 25° appear to be those of Ruby Kawai;[2] at 18° those of Grüneisen;[3] and at 0° those of Lyle and Hosking.[4] The only measurements at extreme dilution known to us are those of Bousfield[5] at 18° which extend down to 0.0017 *N*.

The best sodium chloride available by purchase was dissolved, filtered through a sintered glass filter, then precipitated in a silica dish by passing hydrochloric acid gas into the solution and dried in a centrifuge. The process, except the filtration, was then repeated and the salt finally dried by ignition to a red heat in a platinum dish. The solutions were made up by weight and the period of flow determined in an Ostwald viscometer, the same instrument used by Jones and Stauffer. The timing was done by the automatic photoelectric cell method developed by Jones and Talley. The results are shown in Tables I and II. The figures for the density are the averages of two or three independent determinations which rarely differed by more than 0.001%, obtained with different pycnometers of approximately 60-ml. capacity.

Unfortunately the density determinations on the 2 *N* solutions were omitted through an oversight, but this figure has been estimated with sufficient precision for the purpose from the data of Baxter and Wallace.[6] The fourth column gives the values of d_ct_c/d_0t_0, which is the average of results obtained with at least two fillings of the viscometer and of several runs on each filling.

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[1] Grinnell Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933); *Physics*, **4**, 215 (1933); Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, **57**, 2041 (1933); **58**, 619 (1936); Grinnell Jones and R. E. Stauffer, *ibid.*, **58**, 2558 (1936).

[2] C. E. Ruby and J. Kawai, *ibid.*, **48**, 1119 (1926).

[3] E. Grüneisen, *Wiss. Abhandl. physik.-tech. Reichsanstalt*, **4**, 245 (1905).

[4] T. R. Lyle and R. Hosking, *Phil. Mag.*, **3**, 487 (1902).

[5] W. R. Bousfield, *Phil. Trans.*, **206A**, 101 (1906).

[6] G. P. Baxter and C. C. Wallace, THIS JOURNAL, **38**, 83 (1916).

TABLE I

DENSITY AND RELATIVE VISCOSITY OF SODIUM CHLORIDE SOLUTIONS IN WATER AT 25°

Concn., c	Density d^{25}_4	$\frac{d_c t_c}{d_0 t_0}$	Relative viscosity	$\frac{\eta - 1}{c}$	Jones and Dole equations Simple $\Delta\varphi \times 10^5$	Extended $\Delta\varphi \times 10^5$
0.002	0.99716	1.00043	1.00043	0.21	0	0
.005	.99728	1.00080	1.00081	.16	+ 2	+ 1
.010	.99749	1.00145	1.00146	.146	− 5	− 7
.02	.99790	1.00257	1.00259	.130	− 12	−16
.05	.99913	1.00540	1.00544	.108	− 7	−15
.1	1.00121	1.00988	1.00995	.099	+ 2	−13
.2	1.00528	1.01861	1.01874	.0937	+ 19	− 2
.5	1.01735	1.04570	1.04603	.0921	+ 7	+ 1
1.0	1.03708	1.09511	1.09582	.0958	− 208	+ 4
2.0021	(1.07527)	1.21716	1.21886	.1094	−1238	− 1
(2.0)			(1.2186)			

	Range of validity, N	Average deviation, %
Root equation $d^{25}_4 = 0.997074 + 0.041882\,c - 0.001878\,c^{3/2}$	1	0.0004
Jones and Dole equations		
$\eta = 1 + 0.00670\sqrt{c} + 0.07866\,c$	0.2	.003
$\eta = 1 + 0.00670\sqrt{c} + 0.07620\,c + 0.01291\,c^2$	1.0	.005
$\varphi = 1 - 0.00618\sqrt{c} - 0.07913\,c$	0.5	.005
$\varphi = 1 - 0.00618\sqrt{c} - 0.07729\,c - 0.004005\,c^2$	2.0	.007

TABLE II

DENSITY AND RELATIVE VISCOSITY OF SODIUM CHLORIDE SOLUTIONS AT 0°

Concn., c	Density d^{25}_4	$\frac{d_c t_c}{d_0 t_0}$	Relative viscosity	$\frac{\eta - 1}{c}$	Jones and Dole equations Simple $\Delta\varphi \times 10^5$	Extended $\Delta\varphi \times 10^5$
0.002	0.99996	1.00037	1.00037	0.18	− 12	−12
.005	1.00010	1.00037	1.00037	.073	+ 7	+ 7
.01	1.00032	1.00072	1.00072	.072	− 2	− 4
.02	1.00078	1.00126	1.00126	.063	− 13	−16
.05	1.00211	1.00211	1.00211	.042	+ 11	+ 8
.1	1.00438	1.00382	1.00382	.038	+ 3	−35
.2	1.00877	1.00692	1.00691	.0345	− 3	+40
.5022	1.02194	1.01907	1.01906	.0380	− 343	+51
(.5)			(1.01895)			
1.00588	1.04308	1.04898	1.04900	.0487	−1803	−53
(1.0)			(1.04858)			
2.01766	(1.08362)	1.14730	1.14750	.0731	−7372	+10
(2.0)			(1.14534)			

	Range of validity, N	Average deviation, %
Root equation $d^0_4 = 0.99987 + 0.04605\,c - 0.00307\,c^{3/2}$	1	0.001
Jones and Dole equations		
$\eta = 1 + 0.00448\sqrt{c} + 0.02438\,c$	0.2	.008
$\eta = 1 + 0.00448\sqrt{c} + 0.018923\,c + 0.025284\,c^2$	2	.011
$\varphi = 1 - 0.00456\sqrt{c} - 0.02397\,c$	.2	.008
$\varphi = 1 - 0.00456\sqrt{c} - 0.02228\,c - 0.01897\,c^2$	2	.023

The relative viscosity, η, given in Column 4 is obtained from these figures by the application of a small kinetic energy correction.

In a few cases a correction of 0.001 or 0.002% has been applied to the data as given to bring them to the round concentration given in the first column. For the 2 *N* solution at 25° and for the three strongest solutions at 0° this correction is so large that it seemed best to publish the data as actually determined. The corrected figures at the round concentration are given in parentheses.

Interpretation of the Data

The experimental data given above on the density of sodium chloride up to 1 *N* may be expressed with an average deviation of only 0.001% by the equations having the form suggested by Root.[7]

$$d^{25}_4 = 0.997074 + 0.041882c - 0.001878c^{3/2}$$
$$d^{0}_4 = 0.99987 + 0.04605c - 0.00307c^{3/2}$$

The fifth column shows that the "Grüneisen Effect" is shown by sodium chloride although it is not so pronounced as has been observed with salts of a higher valence type.

The results for the viscosity at 25° can be expressed by the equation $\eta = 1 + 0.00670\sqrt{c} + 0.07866\ c$ up to 0.2 N with an average deviation of only 0.003%. By adding a term proportional to the square of the concentration the equation which is shown at the bottom of Table I may be obtained which fits the data with an average deviation of 0.005% up to 1 N. If the results are expressed in terms of fluidity, φ, instead of viscosity there is a slight improvement in that the simple two-parameter equation holds up to 0.5 N and the extended three-parameter equation holds up to 2 N.

At 0° we find that as usual the relative viscosity is less than at 25°. Here there is little to choose between the equations expressed in terms of viscosity or of fluidity. The average deviations are slightly greater than at 25°, probably because of the greater difficulty in maintaining temperature control during the hot summer weather when this work was done.

The coefficient of the square root term (A) computed by the Falkenhagen and Vernon[8] equation is 0.0060 at 25° and 0.0056 at 0°, whereas the experimentally determined values are 0.0067 and 0.0045, respectively. The agreement is not quite as good as has been found in several other cases, especially at 0°.

Summary

1. The absolute density and relative viscosity of many aqueous solutions of sodium chloride have been determined at 0 and 25°, covering the range of concentration from 0.002 to 2 N.

2. The density of these solutions as a function of the concentration can be expressed by the Root equation, and the viscosity by the Jones and Dole equation.

CAMBRIDGE, MASS. RECEIVED JANUARY 14, 1937

[7] W. C. Root, THIS JOURNAL, **55**, 850 (1933).

[8] H. Falkenhagen and E. L. Vernon, *Physik. Z.*, **33**, 140 (1932).

[CONTRIBUTION FROM THE METALLURGICAL DIVISION, U. S. BUREAU OF MINES]

The Heat Capacities of Molybdenite and Pyrite at Low Temperatures[1]

BY C. TRAVIS ANDERSON[2]

In previous papers[3] the writer has presented low temperature thermal data on manganese sulfide, ferrous sulfide, calcium sulfide and the sulfides of copper and lead. The present paper deals with the heat capacities of molybdenite and pyrite.

The methods, apparatus and accuracy have been described previously.[4]

Materials

Both samples used in this investigation were naturally occurring minerals. The pyrite used was taken from one large specimen. It was broken, and samples that did not show particles of quartz or discoloration were selected. The material was then crushed and screened, the fines being discarded. Analysis of the sample for iron content indicated a purity of 99.24% FeS_2. The only detectable impurity was 0.02% SiO_2. A 301.4-g. sample with a density of 4.951 at 22.4° was studied.

The sample of molybdenite consisted of laminated flakes about 5 mm. in diameter. Since they could not be crushed, the sample was put through a food chopper and screened to size. The only impurities found in the sample were 0.31% FeS_2 and 0.53% SiO_2, which were corrected for in the specific heat measurements. The calorimeter was filled with 166.4 g., with a density of 4.991 at 20.0°.

The Specific Heats

Specific heat measurements have been made on pyrite from 21.7 to 84°K. by Eucken and Schwers,[5] and three points have been measured by

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant physical chemist, Metallurgical Division, U. S. Bureau of Mines, Berkeley, California.

[3] Anderson, THIS JOURNAL, **53**, 476 (1931); **54**, 107 (1932).

[4] Anderson, *ibid.*, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).

[5] Eucken and Schwers, *Ber. deut. physik. Ges.*, **15**, 582 (1913).

Ewald.[6] No previous low temperature measurements have been reported on molybdenite. The results obtained in this Laboratory on these two sulfides, expressed in gram calories (15°) per gram formula weight, as well as a number of Eucken and Schwers' and Ewald's determinations, are shown graphically in Fig. 1. The experimental values for the heat capacities are given in Tables I and II. The calculations were made on the basis of Fe = 55.84, Mo = 96.0 and S = 32.06.

TABLE I

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF PYRITE (FeS_2)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
55.8	1.004	121.2	6.467	252.6	13.91
60.5	1.275	144.2	8.356	273.3	14.40
68.4	1.802	180.1	10.72	286.9	14.60
82.3	2.859	204.9	12.01	292.8	14.77
100.0	4.484	227.5	12.90	297.0	14.79

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF MOLYBDENITE (MoS_2)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
56.1	2.297	100.2	5.764	220.4	13.28
60.7	2.601	118.7	7.368	249.5	14.14
70.5	3.264	143.5	9.318	279.7	14.88
80.6	3.944	161.3	10.57	292.3	15.08
		189.5	11.78		

Calculation of Entropies

The conventional method was used in calculating the entropy. The heat capacity curves were extrapolated from the lower points and coincided with Debye functions having the parameters (Θ) for FeS_2, 421, and MoS_2, 280. The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weight of these sulfides.

$$C_{FeS_2} = D\left(\frac{421}{T}\right) + 2E\left(\frac{532}{T}\right)$$

$$C_{MoS_2} = D\left(\frac{280}{T}\right) + 2E\left(\frac{528}{T}\right)$$

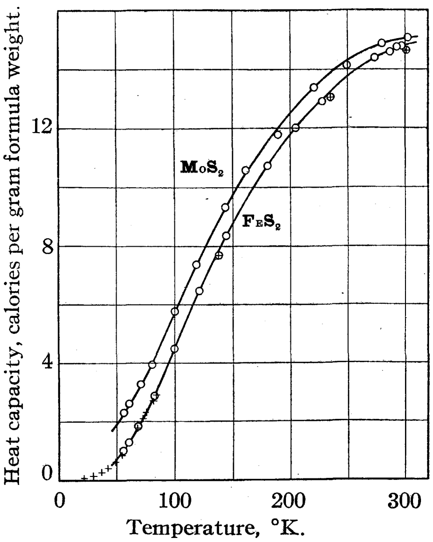

Fig. 1.—The heat capacities of pyrite and molybdenite, in calories per gram formula weight: ○, Anderson; +, Eucken and Schwers; ⊕, Ewald.

The results of the entropy calculations from the experimental heat capacity data and the function sums are given in Table III.

TABLE III

	FeS_2	MoS_2
Extrap. (0–56.2), °K.	0.34	0.99
Graph (56.2–298.1), °K.	12.38	14.07
$S°_{298.1}$ graphical	12.7 ± 0.1	15.1 ± 0.2
$S°_{298.1}$ calcd. from functions	12.7	15.0

Summary

The heat capacities of FeS_2 (pyrite) and MoS_2 (molybdenite) from about 56 to 300°K. have been measured and their corresponding entropies determined as 12.7 and 15.1, respectively.

BERKELEY, CALIF. RECEIVED DECEMBER 30, 1936

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[6] Ewald, *Ann. Physik*, [4], **44**, 1213 (1914).

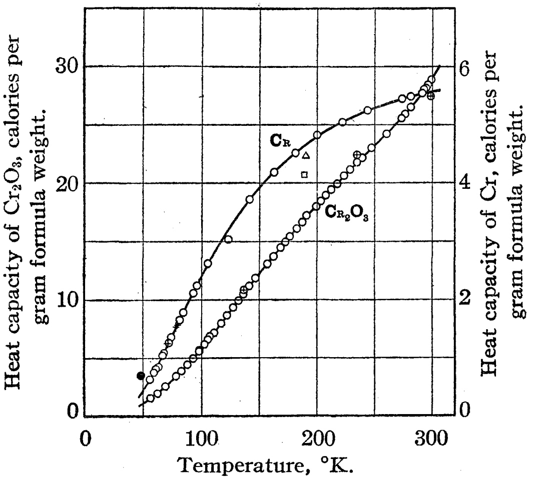
[CONTRIBUTION FROM THE METALLURGICAL DIVISION, U. S. BUREAU OF MINES]

The Heat Capacities of Chromium, Chromic Oxide, Chromous Chloride and Chromic Chloride at Low Temperatures[1]

BY C. TRAVIS ANDERSON[2]

The work presented in this paper is a part of the program for a systematic thermodynamic study of chromium and some of its compounds that the U. S. Bureau of Mines has been conducting for a number of years. This report deals with the heat capacities and entropies of chromium, chromic oxide, chromous chloride and chromic chloride. A manuscript, the "Chemistry of the Anhydrous Chlorides of Chromium," is in course of publication as a Bureau bulletin.

The methods, apparatus and accuracy have been described previously.[3]



○, Anderson; ●, Dewar; □, Richards and Jackson; △, Nordmeyer and Bernoulli; +, Simon and Ruhemann; ⊕, Russell.

Fig. 1.—The heat capacities of chromium and chromic oxide, in calories per gram formula weight.

Materials

The sample of chromium metal, which was prepared electrolytically, was obtained for this Laboratory through the courtesy of Dr. John Chipman, who obtained it from Mr. Marsh of the Hoskins Manufacturing Company. It was carefully hand-picked to obtain particles of uniform color without a coating of chromic oxide. The selected particles were placed in a silica flask, evacuated and heated to 1100° to remove any hydrogen that might have been present. An analysis of the sample, after this treatment, by Dr. Chipman showed it to contain 0.65% oxygen and no nitrogen. This oxygen was assumed to be present in the form of chromic oxide and was corrected for in the heat capacity of the chromium. The calorimeter was filled with 401.6 g.

The chromic oxide was Kahlbaum highest quality, containing no detectable impurity. It was compressed into pellets, placed in a silica flask, evacuated and heated. Measurements were made on a 145.6-g. sample.

The author is indebted to H. A. Doerner and W. C. McGavock for the preparation of the anhydrous chlorides of chromium. The chromic chloride was prepared by passing chlorine gas through a mixture of chromic oxide and carbon at about 800°. The resulting vapor was condensed, removed from the condenser and redistilled in an atmosphere of dry chlorine containing small amounts of carbon tetrachloride vapor. The product consisted of brilliant violet, flat, thin flakes about 2 mm. in diameter. It was compressed into pellets, broken to size and dried by passing dry chlorine containing a little carbon tetrachloride through the chromic chloride at about 300°. It was finally evacuated to remove any excess chlorine, after which a 113.6-g. sample was transferred to the calorimeter out of contact with air.

The chromous chloride used in this investigation was prepared from a portion of the pure chromic chloride described above by reduction with hydrogen containing a small amount of hydrogen chloride to prevent reduction of the chloride to metal. The resulting chloride was grayish-white and extremely hygroscopic. The material was transferred from the reaction flask to the calorimeter out of contact with air; 111.8 g. of this sample was used in the specific heat measurements.

The Specific Heats

A number of investigators[4] have made specific heat measurements on chromium metal. With the exception of those of Simon and Ruhemann, these determinations are mean specific heats. The various values obtained by these investigators on chromium are shown in Fig. 1.

Russell[5] has made measurements on the specific heat of chromic oxide ranging from 137 to 299°K. These values are also shown in Fig. 1.

Trapeznikowa, Schubnikow and Miljutin[6] have recently measured the specific heat of chromic chloride from 12 to 130°K. Their results are definitely higher than those of the present work.

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(1) Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

(2) Assistant physical chemist, Metallurgical Division, U. S. Bureau of Mines, Berkeley, California.

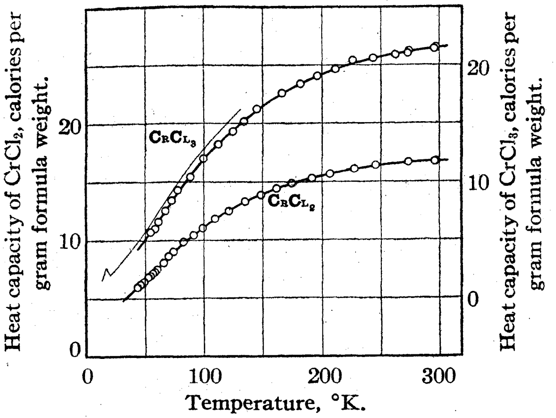
(3) Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).

(4) Dewar, *Proc. Roy. Soc.* (London), **A89**, 158 (1913); Richards and Jackson, *Z. physik. Chem.*, **70**, 414 (1910); Nordmeyer and Bernoulli, *Verhand. deut. physik. Ges.*, **9**, 175 (1907); Simon and Ruhemann, *Z. physik. Chem.*, **129**, 321 (1927).

(5) Russell, *Physik. Z.*, **13**, 59 (1912).

(6) Trapeznikowa, Schubnikow and Miljutin, *Phys. Z. Sowjetunion*, **9**, 237 (1936).

Over the range of 56 to 112°K. they average 0.82 cal./deg. higher. These values are represented graphically in Fig. 2. From the description of their apparatus it appears that their measurements have been sufficiently accurate and their temperature scale should not be in error. However, the sample they used might have contained water, as the apparently insoluble chromic chloride is capable of absorbing up to 3% water in sixty minutes of contact with laboratory air as shown by Crespi.[7] It appears probable, since the difference between these two curves is constant over the range of 56 to 112°K., that some systematic error is the cause of the discrepancy.



-O-, Anderson; —— $CrCl_3$, Trapeznikowa, Schubnikow and Miljutin.

Fig. 2.—The heat capacities of chromous chloride and chromic chloride, in calories per gram formula weight.

No previous low temperature measurements have been reported on chromous chloride. The results obtained in this Laboratory on the heat capacities of chromium and chromic oxide expressed in gram calories (15°) per gram formula weight are shown graphically in Fig. 1 and the values for chromous and chromic chlorides are represented graphically in Fig. 2. The experimental determinations of the heat capacities for chromium are given in Table I, the values for chromic oxide up to about 270°K. are given in Table II, while Table III shows the values for the heat capacities from about 270° to 340°K. with the temperature rise (ΔT) of the determinations. This table is represented graphically in the upper figure in Fig. 3. The experimental values for the chromous and chromic chlorides are given in Tables IV and V. The calculations were made on the basis of Cr = 52.01, O = 16.00 and Cl = 35.457.

TABLE I

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF CHROMIUM

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
56.1	0.634	81.6	1.646	162.9	4.180
59.5	.752	84.8	1.776	181.6	4.508
61.1	.811	93.2	2.114	200.1	4.816
63.5	.851	96.1	2.237	222.1	5.043
66.9	1.042	105.8	2.623	244.1	5.244
68.0	1.087	123.1	3.027	274.0	5.442
72.4	1.256	141.6	3.715	281.5	5.479
74.2	1.357			291.1	5.542

After calculating and plotting the heat capacity curve for chromic oxide it was noted that the points above the ice point appeared to deviate from the smooth curve which was drawn through the lower points. Further measurements were made which showed this deviation was due to an anomaly. The peak of the curve appears at about 305°K. No measurements were made on the energy necessary to heat the chromic

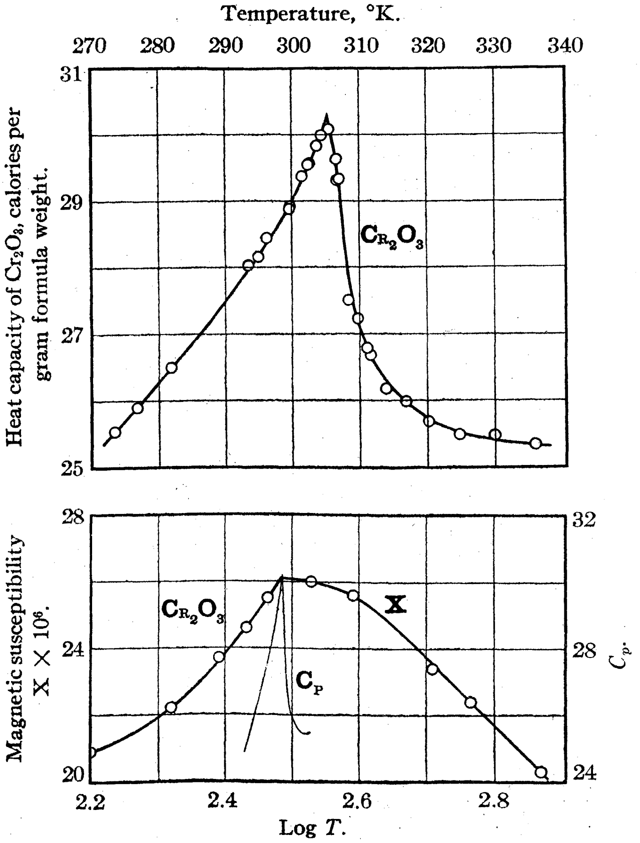


Fig. 3.—The heat capacity and magnetic susceptibility of chromic oxide.

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(7) Crespi, *Anales soc. españ. fís. quím.*, **26**, 152 (1928).

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CHROMIC OXIDE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
56.3	1.504	117.2	7.951	187.4	16.62
62.5	1.958	122.2	8.625	192.1	17.20
69.4	2.577	127.4	9.312	199.6	17.98
78.5	3.417	132.1	9.903	203.6	18.43
83.0	3.866	136.4	10.45	207.9	18.94
88.1	4.410	141.7	11.16	212.6	19.43
93.0	4.962	147.0	11.83	217.9	19.94
98.1	5.562	157.4	13.07	223.7	20.61
98.6	5.629	162.2	13.69	229.0	21.14
102.9	6.169	168.5	14.45	234.9	21.75
105.9	6.587	172.7	14.93	239.7	22.15
107.4	6.729	176.6	15.41	247.6	23.00
111.1	7.131	182.6	16.09	260.4	24.20

TABLE III

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CHROMIC OXIDE

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
273.3	3.610	25.54	306.6	4.518	29.63
276.7	4.907	25.90	306.7	3.954	29.31
281.8	4.727	26.50	307.0	2.419	29.33
293.4	3.161	28.03	308.3	2.579	27.50
294.9	3.004	28.16	309.7	2.537	27.23
296.2	3.829	28.44	311.1	2.607	26.79
299.6	2.632	28.88	311.6	4.736	26.68
299.7	2.563	28.92	313.9	2.629	26.18
301.5	4.017	29.37	316.8	2.612	25.99
302.4	2.547	29.54	320.2	5.204	25.69
302.6	2.496	29.56	324.8	5.163	25.47
303.7	2.554	29.83	329.9	4.996	25.48
304.4	2.399	29.99	335.6	3.892	25.34
305.5	2.436	30.08			

TABLE IV

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CHROMOUS CHLORIDE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
43.6	5.987	70.0	8.620	162.4	14.41
46.4	6.207	74.3	9.010	174.3	14.89
49.5	6.430	82.5	9.857	191.2	15.29
52.9	6.847	91.1	10.42	206.8	15.65
54.7	6.958	99.0	11.04	227.3	16.08
56.7	7.184	109.8	11.85	245.3	16.37
58.2	7.320	121.8	12.50	273.5	16.67
60.2	7.518	134.9	13.30	295.1	16.73
65.9	8.098	148.3	13.89	296.1	16.76

TABLE V

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CHROMIC CHLORIDE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.4	5.705	112.0	13.21	211.2	19.64
58.4	6.020	123.3	14.31	225.6	20.42
61.2	6.597	132.8	15.14	243.0	20.60
67.4	7.521	144.9	16.24	261.9	20.90
72.4	8.398	165.9	17.58	272.6	21.04
77.7	9.300	181.6	18.40	273.5	21.24
88.4	10.41	195.7	19.06	295.4	21.46
99.8	11.99			296.9	21.59

oxide through this transition. Honda and Sone[8] measured the magnetic susceptibility of chromic oxide over a wide temperature range. A graphical representation of a portion of their results is shown in the lower figure of Fig. 3. The magnetic susceptibility is plotted against the logarithm of the absolute temperature. The temperature of the break in their curve approximates very closely the peak in the specific heat curve which is drawn in for comparison.

The calorimeter was cooled to below 300°K. five times, after which measurements were made both below and above the transition temperature. The curve was found to be perfectly reproducible.

Calculation of Entropies

The entropies were calculated by the usual graphical method of plotting the heat capacity against the logarithm of the temperature. In the case of the chromic chloride the results of Trapeznikowa, Schubnikow and Miljutin were used on the lower portion of the curve. Since there appeared to be a constant difference of 0.82 cal. over the range of 56 to 112°K. between their measurements and those presented in this report, it was assumed that this difference would exist below 56°K. Accordingly, their results were used on the lower end of the curve to attempt to obtain a more reliable value for the entropy than if they had not been used. If their data are extrapolated to room temperature from their highest point, assuming a 1.0 calorie difference between the two curves over this region, an entropy value of 31.2 units is obtained.

The experimental heat capacity curves coincided at low temperature with Debye functions having the following parameters (Θ): for chromium, 488; chromic oxide, 362; chromous chloride, 82; and chromic chloride, 100. Simon and Ruhemann gave a value for $\Theta = 486 \pm 8$, after correcting the 92% chromium they used for the impurities it contained. This is in excellent accord with the value of 488 obtained in this work.

Obviously, no combination of Debye and Einstein functions can be made to fit the experimental curve for the heat capacity of chromic chloride. Similarly, the function sum cannot be expected to fit the chromic oxide near room temperature as the transition begins to have an influence on the heat capacity even as low as

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(8) Honda and Sone, *Science Rep. Tôhoku Imp. Univ.*, **3**, 223 (1914).

200°. For this reason one may expect the function sum in this case to give a considerably lower entropy value than that obtained by the more accurate graphical method.

The following combinations were found to fit the experimental data on chromic oxide and chromous chloride to above 100°.

$$C_{Cr_2O_3} = D\left(\frac{362}{T}\right) + 2E\left(\frac{470}{T}\right) + 2E\left(\frac{780}{T}\right)$$

$$C_{CrCl_2} = D\left(\frac{82}{T}\right) + E\left(\frac{226}{T}\right) + E\left(\frac{444}{T}\right)$$

TABLE VI

ENTROPY DATA

	Cr	Cr_2O_3	$CrCl_3$
Extrap. (0–56.2), °K.	0.22	0.53	3.96
Graph (56.2–298.1), °K.	5.46	18.84	24.24
$S°_{298.1}$ graphical	5.68 ± 0.05	19.4 ± 0.2	28.2 ± 1.0
$S°_{298.1}$ calcd. from functions		18.0	

	$CrCl_2$
Extrap. (0–44.7), °K.	5.05
Graph (44.7–298.1), °K.	22.36
$S°_{298.1}$ graphical	27.4 ± 0.7
$S°_{298.1}$ calcd. from functions	27.6

Table VI gives the results of the entropy calculations.

Related Thermal Data

Thermal data relating to these materials and the source are given in Table VII.

TABLE VII

THERMAL DATA

	$\Delta H_{298.1}$	$\Delta F°_{298.1}$	$S_{298.1}$ This report	$S_{298.1}$
Cr			5.68	
Cr_2O_3	−288,900[a]	−269,400[c]	19.4	
$CrCl_2$	− 92,750[b]	− 84,008[b]	27.4	29.7[b]
$CrCl_3$	−129,565[b]	−113,253	28.2	31.0[b], 31.2[d]

[a] Roth and Becker, *Z. physik. Chem.*, **A145**, 467 (1930).

[b] Doerner, U. S. Bureau of Mines (in press).

[c] Calculated from $\Delta H_{298.1}$ and entropies.

[d] Trapeznikowa, Schubnikow and Miljutin, *Physik. Z. Sowjetunion*, **9**, 237 (1936).

Summary

The heat capacities of chromium, chromic oxide and chromous and chromic chlorides at low temperatures have been determined and their corresponding entropies calculated as 5.68, 19.4, 27.4 and 28.2, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary Systems $KClO_3$–K_2SO_4–H_2O and $NaClO_3$–Na_2SO_4–H_2O[1]

BY JOHN E. RICCI AND NICHOLAS S. YANICK

Introduction

This study is part of a systematic investigation of ternary systems involving sodium and potassium chlorates, a series of systems of which several examples are already to be found in the literature. No double salts containing sodium chlorate have yet been reported, the only ternary systems studied being $NaClO_3$–Na_2CO_3–H_2O, $NaClO_3$–$NaCl$–H_2O and $NaClO_3$–$KClO_3$–H_2O.[2] Similarly, in the systems involving potassium chlorate that have been investigated, no compounds are found (–H_2O + KCl, K_2CO_3, $NaClO_3$[2]; also +KBr and KI[3]); potassium chlorate however is found to form solid solutions in the systems $KClO_3$–KNO_3–H_2O and $KClO_3$–$TlClO_3$–H_2O.[2]

As for the sulfates in the present systems, while sodium sulfate is known to form both various double compounds and solid solutions with other sodium salts, potassium sulfate, in systems so far studied, forms no double salts with other potassium salts, but does form solid solutions with potassium chromate and potassium molybdate.[2]

In the present investigation potassium chlorate and potassium sulfate show no complex formation, while the sodium salt system forms one double salt, $NaClO_3 \cdot 3Na_2SO_4$. As for the other sodium halogenates, sodium sulfate forms similar compounds with sodium iodate, namely, $NaIO_3 \cdot 3Na_2SO_4$ and $NaIO_3 \cdot 4Na_2SO_4$,[4] while with sodium bromate it forms no definite compound but a solid solution.[5]

Experimental Methods

The experimental procedure was that usually described for similar investigations. Weighed complexes of known composition were brought to equilibrium by stirring in a

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(1) Presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

(2) "International Critical Tables," Vol. IV, 1928.

(3) Author's unpublished data.

(4) Foote and Vance, *Am. J. Sci.*, **19**, 203 (1930).

(5) Ricci, THIS JOURNAL, **57**, 805 (1935).

large water-bath in which the temperature was maintained constant to ±0.02°. The time required for attainment of equilibrium was determined by analysis, and varied from a few days in the case of the potassium salts, to several weeks in some cases of the sodium salt system. The order of mixing of the components, and the process of "seeding" or inoculation for required phases, had to be varied in accordance with the phase sought. All the solid phases involving sodium sulfate show a considerable tendency to persist in metastable equilibrium, and these metastable phases sometimes change only very slowly to the stable form even with repeated seeding. The densities reported for some of the isotherms were obtained by means of volumetric pipets calibrated for delivery.

The method of analysis of the saturated solution was the same in both systems. In one sample of the solution the chlorate was determined by a volumetric method; in another sample the total solid was determined by evaporation to dryness at 100° followed by 250°; and the sulfate was then calculated by difference. For the chlorate determination, the method of Peters and Deutschländer[6] was used: to the chlorate sample (containing about 0.11 g. of ClO_3^-) is added a definite volume (50 cc.) of 0.05 *M* arsenious oxide solution (previously standardized against pure sodium chlorate by the same procedure); after the addition of a trace of potassium bromide, the solution is acidified strongly with hydrochloric acid and boiled for ten minutes. The excess arsenious oxide is then titrated by Györy's method,[7] by means of 0.033 *M* potassium bromate solution (previously compared with the arsenite solution) using indigo sulfonic acid as indicator.

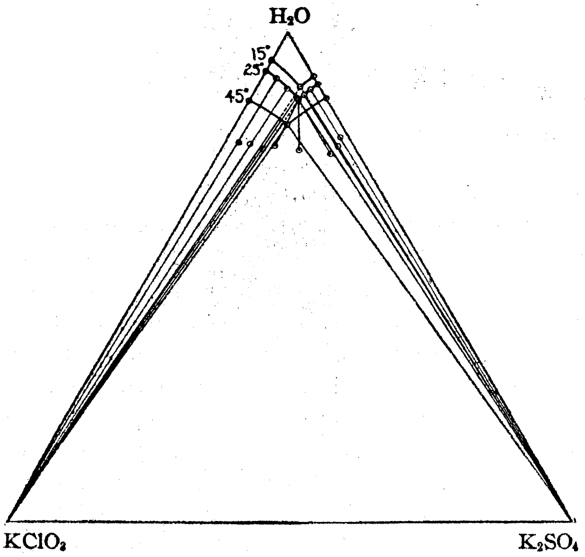

Fig. 1.—System $KClO_3$–K_2SO_4–H_2O.

For the identification of known solid phases, microscopic examination and algebraic extrapolation of tie-lines sufficed. The determination of the formula of the new double salt however was more difficult. Direct analysis of the crystals was not successful; the salt is always incongruently soluble; the crystals were very small, always contaminated with a mother liquor highly concentrated with respect to sodium chlorate, and readily decomposed by washing; even centrifuged residues contained large amounts of mother liquor or of its crystallized salts. Dehydration of residues over various drying agents showed no break in the drying–time curve, so that the solid appeared to be anhydrous. This however is also very clearly seen from the definite convergence of all the tie-lines for complexes giving the double salt as single solid phase, on a point on the $NaClO_3$–Na_2SO_4 side of the triangle. Considering the wide spread of the solubility curve of the double compound at the various temperatures employed, and the fact that the compound is anhydrous, these extrapolations constitute a sufficiently accurate determination of the formula of the double salt. Extrapolating 38 such tie-lines, covering the three different temperatures at which the double salt was obtained, to the point on the base of the triangle representing the formula $NaClO_3 \cdot 3Na_2SO_4$ (containing 80.01% Na_2SO_4), the average absolute error of the extrapolations was 0.63% and the average algebraic error only +0.06%, in sodium sulfate. A further check on the formula was made by means of a method due to Bijlert;[8] two different complexes, of definite compositions, calculated to give the double salt (in metastable equilibrium) were made up, with the addition of a definite amount of a fourth component, sodium chloride, to each. By means of a complete analysis, when equilibrium had been reached, both of the saturated solution and of a wet residue, the amount of mother liquor contained in the wet residue was calculated through the sodium chloride content, thus making possible quite an accurate determination of the composition of the double salt. The results again gave an anhydrous compound, with 80.45 and 80.24% Na_2SO_4 in the two different runs, as compared with 80.01% calculated from the formula $NaClO_3 \cdot 3Na_2SO_4$.

Results

System $KClO_3$–K_2SO_4–H_2O.—The results on this system are given in Table I, and the curves for the three temperatures are shown in condensed form in Fig. 1. No complex formation is observed, the only solid phases being potassium chlorate and potassium sulfate.

System $NaClO_3$–Na_2SO_4–H_2O.—The experimental data for the four temperatures studied (75, 45, 25 and 15°) are presented in Tables II–V, the isotherms being shown graphically in Figs. 2–5. (In these tables, the abbreviation "D.S." stands for "double salt," while (m) indicates metastable phases.)

75° Isotherm.—The solid phases at this temperature are Na_2SO_4 for the curve a-b, $NaClO_3 \cdot 3Na_2SO_4$ for b-c, and $NaClO_3$ for c-d. As may be seen from the diagram, the double salt exists as a stable phase over a short range of variation of

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(6) Peters and Deutschländer, *Apoth. Z.*, 594 (1926); see Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, New York, N. Y., 1929, p. 465.

(7) Györy, *Z. anal. Chem.*, **32**, 415 (1893).

(8) Bijlert, *Z. physik. Chem.*, **8**, 343 (1891); see also Bancroft, *J. Phys. Chem.*, **6**, 178 (1902).

TABLE I

$KClO_3$–K_2SO_4–H_2O

Original complex, wt. %		Satd. soln., wt. %			
$KClO_3$	K_2SO_4	$KClO_3$	K_2SO_4	Density	Solid phase
			45°		
0.00	...	0.00	13.53		K_2SO_4
12.23	19.51	9.80	9.13		$K_2SO_4 + KClO_3$
21.04	7.99	9.80	9.12		$K_2SO_4 + KClO_3$
Av. (of 2)		9.80	9.13		$K_2SO_4 + KClO_3$
...	0.00	13.90	...		$KClO_3$
			25°		
0.00	...	0.00	10.76	1.083	K_2SO_4
1.60	20.02	1.80	9.93	1.089	K_2SO_4
2.89	20.42	3.30	9.43	1.099	K_2SO_4
4.95	19.80	4.95	8.66	1.102	$K_2SO_4 + KClO_3$
10.03	14.01	4.96	8.62	1.100	$K_2SO_4 + KClO_3$
16.03	9.11	4.96	8.62	1.099	$K_2SO_4 + KClO_3$
Av. (of 3)		4.96	8.64	1.100	$K_2SO_4 + KClO_3$
16.51	7.20	5.06	8.19	1.099	$KClO_3$
18.04	4.85	5.77	5.57	1.080	$KClO_3$
20.06	2.35	6.72	2.73	1.063	$KClO_3$
...	0.00	7.897	0.00	1.048	$KClO_3$
			15°		
0.00	...	0.00	9.258	1.076	K_2SO_4
3.51	20.02	3.29	7.86	1.085	$K_2SO_4 + KClO_3$
18.01	7.01	3.29	7.86	1.084	$K_2SO_4 + KClO_3$
Av. (of 2)		3.29	7.86	1.085	$K_2SO_4 + KClO_3$
...	0.00	5.676	0.00	1.032	$KClO_3$

TABLE II

$NaClO_3$–Na_2SO_4–H_2O AT 75°

Original complex, wt. %		Satd. soln., wt. %		
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	Solid phase
0.00	...	0.00	30.33	Na_2SO_4
5.00	39.96	6.26	24.70	Na_2SO_4
23.98	21.10	27.19	10.56	Na_2SO_4
33.07	11.98	35.05	6.88	Na_2SO_4
42.22	10.06	45.51	3.19	Na_2SO_4
46.11	10.03	50.00	2.39	Na_2SO_4
44.98	14.99	51.85	2.09	Na_2SO_4
50.91	6.88	53.63	1.92	Na_2SO_4
51.71	7.02	54.59	1.73	Na_2SO_4
52.11	8.06	55.78	1.57	Na_2SO_4 + D.S.
52.98	6.89	55.62	1.51	Na_2SO_4 + D.S.
53.08	7.04	55.74	1.49	Na_2SO_4 + D.S.
Av. (of 3)		55.71	1.52	Na_2SO_4 + D.S.
55.14	6.09	57.81	1.61	Na_2SO_4 (m)
39.76	10.88	41.42	5.11	D.S. (m)
40.68	12.01	42.98	4.50	D.S (m)
44.98	8.44	46.82	3.27	D.S. (m)
47.80	7.92	49.91	2.51	D.S. (m)
48.88	7.97	51.15	2.28	D.S. (m)
50.73	6.95	52.84	1.94	D.S. (m)
51.09	6.98	53.20	1.99	D.S. (m)
53.49	5.02	54.90	1.84	D.S. (m)
54.17	6.11	56.25	1.62	D.S.
54.99	6.02	57.26	1.30	D.S.
56.63	5.00	58.34	1.37	D.S.
56.83	6.89	59.79	1.05	D.S.
58.13	5.00	60.10	1.14	D.S.
59.30	6.89	60.56	1.05	D.S. + $NaClO_3$
62.19	3.01	60.80	0.93	D.S. + $NaClO_3$
Av. (of 4)		60.73	1.00	D.S. + $NaClO_3$
...	0.00	61.40	0.00	$NaClO_3$

TABLE III

$NaClO_3$–Na_2SO_4–H_2O AT 45°

Original complex, wt. %		Satd. soln., wt. %		
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	Solid phase
0.00	...	0.00	32.08	Na_2SO_4
15.09	30.07	17.88	17.52	Na_2SO_4
25.59	25.60	31.36	9.03	Na_2SO_4
33.22	14.33	36.12	6.87	Na_2SO_4
34.62	14.28	37.97	6.09	Na_2SO_4
35.01	20.05	41.84	4.61	Na_2SO_4
41.76	12.20	45.88	3.55	Na_2SO_4
45.12	10.03	48.64	2.80	Na_2SO_4
46.14	10.07	49.76	2.53	Na_2SO_4 + D.S.
44.15	15.05	49.66	2.60	Na_2SO_4 + D.S.
Av. (of 2)		49.71	2.57	Na_2SO_4 + D.S.
49.05	7.01	51.46	2.38	Na_2SO_4 (m)
20.18	21.28	20.10	18.68	D.S. (m)
27.78	15.92	28.23	12.66	D.S. (m)
32.94	13.03	33.73	9.13	D.S. (m)
36.96	10.04	37.67	7.00	D.S. (m)
39.03	10.04	40.14	5.85	D.S. (m)
42.14	9.01	43.56	4.45	D.S. (m)
44.99	6.98	46.18	3.57	D.S. (m)
47.03	8.96	49.48	2.67	D.S. (m)
47.17	10.04	50.22	2.40	D.S.
48.59	10.06	51.79	2.21	D.S.
49.13	10.04	52.57	1.97	D.S.
49.83	9.97	53.16	1.80	D.S. + $NaClO_3$
55.32	6.06	53.02	1.85	D.S. + $NaClO_3$
60.95	2.11	53.12	1.70	D.S. + $NaClO_3$
Av. (of 5)		53.10	1.77	D.S. + $NaClO_3$
...	0.00	54.59	0.00	$NaClO_3$

TABLE IV

$NaClO_3$–Na_2SO_4–H_2O AT 25°

Original complex, wt. %		Satd. soln., wt. %		
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	Solid phase
0.00	...	0.00	21.78	$Na_2SO_4 \cdot 10H_2O$
5.13	24.11	6.58	18.20	$Na_2SO_4 \cdot 10H_2O$
10.04	21.02	12.30	15.77	$Na_2SO_4 \cdot 10H_2O$
15.09	18.99	18.05	13.90	$Na_2SO_4 \cdot 10H_2O$
20.98	15.99	23.45	12.64	$Na_2SO_4 \cdot 10H_2O$
25.94	13.76	27.36	12.06	$Na_2SO_4 \cdot 10H_2O$
27.50	14.00	28.92	12.21	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
27.37	14.74	28.87	12.03	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
Av. (of 2)		28.90	12.12	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
22.80	19.32	29.29	12.23	$Na_2SO_4 \cdot 10H_2O$ (m)
26.32	15.50	29.52	12.20	$Na_2SO_4 \cdot 10H_2O$ (m)
27.46	15.52	29.90	12.25	$Na_2SO_4 \cdot 10H_2O$ (m) + D.S. (m)
26.30	18.34	29.89	12.27	$Na_2SO_4 \cdot 10H_2O$ (m) + D.S. (m)
Av. (of 2)		29.90	12.26	$Na_2SO_4 \cdot 10H_2O$ (m) + D.S. (m)
0.00	...	0.00	33.97	Na_2SO_4 (m)

TABLE IV (*Concluded*)

Original complex, wt. %		Satd. soln., wt. %		Solid phase
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	
5.06	40.13	6.03	28.62	Na_2SO_4 (m)
14.92	30.09	17.09	19.89	Na_2SO_4 (m)
26.99	15.96	28.02	12.53	Na_2SO_4 (m)
29.20	18.89	32.47	9.86	Na_2SO_4
34.89	15.02	38.07	7.21	Na_2SO_4
38.04	15.05	42.39	5.37	Na_2SO_4
39.91	15.01	44.76	4.60	Na_2SO_4
44.56	8.07	46.28	4.02	Na_2SO_4 + D.S.
45.84	5.06	46.26	4.02	Na_2SO_4 + D.S.
46.01	5.02	46.40	3.99	Na_2SO_4 + D.S.
Av. (of 3)		46.31	4.01	Na_2SO_4 + D.S.
25.00	19.02	25.26	15.72	D.S. (m)
26.83	16.94	27.00	14.75	D.S. (m)
30.30	15.19	30.80	11.90	D.S. (m)
31.07	15.04	31.65	11.35	D.S. (m)
31.92	15.09	32.71	10.65	D.S. (m)
33.19	13.48	33.85	9.93	D.S. (m)
33.49	14.05	34.36	9.61	D.S. (m)
35.00	13.08	36.08	8.56	D.S. (m)
36.07	13.06	37.31	7.91	D.S. (m)
39.10	9.05	39.75	6.70	D.S. (m)
39.80	11.04	41.19	5.99	D.S. (m)
43.03	8.06	44.10	4.76	D.S. (m)
42.49	11.03	44.55	4.75	D.S. (m)
45.03	14.98	46.57	3.83	D.S. + $NaClO_3$
46.98	5.50	46.63	3.89	D.S. + $NaClO_3$
53.24	4.03	46.68	3.83	D.S. + $NaClO_3$
Av. (of 7)		46.62	3.87	D.S. + $NaClO_3$
48.67	4.55	46.63	3.88	Na_2SO_4 (m) + $NaClO_3$ (m)
48.46	6.20	46.64	3.85	Na_2SO_4 (m) + $NaClO_3$ (m)
Av. (of 2)		46.64	3.86	Na_2SO_4 (m) + $NaClO_3$ (m)
54.99	2.40	47.62	2.80	$NaClO_3$
...	0.00	50.14	0.00	$NaClO_3$

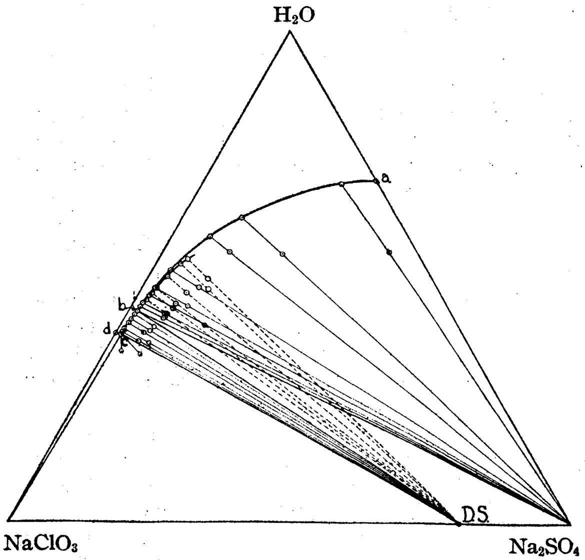

Fig. 2.—75° Isotherm: $NaClO_3$–Na_2SO_4–H_2O.

TABLE V

$NaClO_3$–Na_2SO_4–H_2O AT 15°

Original complex, wt. %		Satd. soln., wt. %		Density	Solid phase
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4		
0.00	...	0.00	11.60	1.106	$Na_2SO_4 \cdot 10H_2O$
15.02	15.00	19.86	5.52	1.200	$Na_2SO_4 \cdot 10H_2O$
27.01	13.02	34.75	4.06	1.323	$Na_2SO_4 \cdot 10H_2O$
31.93	9.54	36.89	4.15	1.348	$Na_2SO_4 \cdot 10H_2O$
35.00	8.49	39.37	4.02	1.372	$Na_2SO_4 \cdot 10H_2O$
36.97	8.02	41.16	3.92		$Na_2SO_4 \cdot 10H_2O$
39.99	6.77	43.07	3.89		$Na_2SO_4 \cdot 10H_2O$
41.20	6.19	43.67	3.90		$Na_2SO_4 \cdot 10H_2O$
41.97	13.08	44.14	4.03	1.422	$Na_2SO_4 \cdot 10H_2O$ + $NaClO_3$
44.96	10.03	44.10	4.09	1.422	$Na_2SO_4 \cdot 10H_2O$ + $NaClO_3$
Av. (of 2)		44.12	4.06	1.422	$Na_2SO_4 \cdot 10H_2O$ + $NaClO_3$
34.51	12.52	35.93	8.91	1.393	Na_2SO_4 (m)
36.49	12.51	38.37	7.98	1.408	Na_2SO_4 (m)
41.93	13.00	41.77	6.52		Na_2SO_4 (m) + $NaClO_3$ (m)
44.93	10.00	41.92	6.36	1.424	Na_2SO_4 (m) + $NaClO_3$ (m)
Av. (of 2)		41.85	6.44	1.424	Na_2SO_4 (m) + $NaClO_3$ (m)
52.00	4.55	42.66	5.59		$NaClO_3$ (m)
55.99	3.00	44.34	3.83	1.422	$NaClO_3$
55.94	1.70	45.86	2.19	1.423	$NaClO_3$
...	0.00	47.91	0.00	1.406	$NaClO_3$

only 5% in respect to sodium chlorate, but its solubility curve has been followed as a metastable equilibrium as far as 41% $NaClO_3$ (a total range of 15% on the diagram). The same behavior is observed at the other temperatures (45 and 25°), where the range of stability is even smaller (3.4

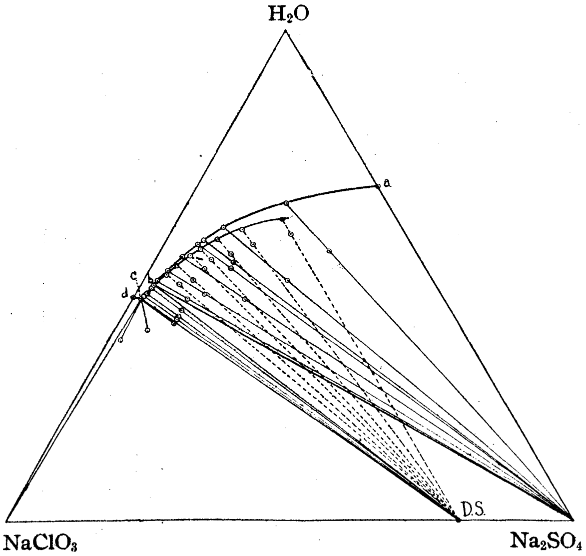

Fig. 3.—45° Isotherm: $NaClO_3$–Na_2SO_4–H_2O.

and 0.3%, respectively); at 45° the total range recorded is 33%, and at 25°, 22%. Possibly these curves could be followed even further, but a point of congruent saturation was not reached in the present work. Another peculiarity of this double compound to be pointed out is the extreme slowness with which the phase, when present in a metastable state (fine, lustrous, needle-shaped crystals) yields, on seeding, to the formation of the stable sodium sulfate. In fact mere seeding never gave a complete change from the metastable to the stable curve. The stable curve for sodium sulfate is obtained only by taking care to prevent seeding with the double salt; otherwise crystals of the latter forming temporarily or accidentally persist in an extraordinary manner.

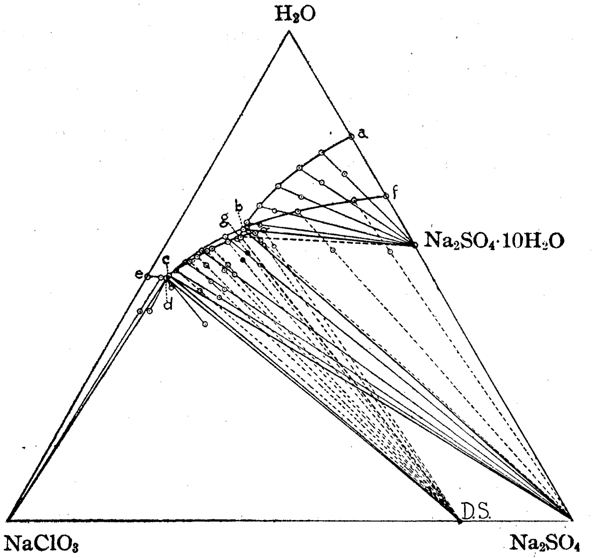

Fig. 4.—25° Isotherm: $NaClO_3$–Na_2SO_4–H_2O.

45° Isotherm.—Phases and general relations just as at 75°.

25° Isotherm.—The stable phases and their solubility curves are as follows: $Na_2SO_4 \cdot 10H_2O$, for a-b; Na_2SO_4 for b-c; $NaClO_3 \cdot 3Na_2SO_4$ for c-d; and $NaClO_3$ for d-e. The curve b-f is the metastable extension of the sodium sulfate solubility curve, point f being the metastable solubility of sodium sulfate at 25°. The double salt curve extends for a considerable distance beside the stable sodium sulfate curve, and meets a metastable extension of a-b at the point g, which is therefore an isothermally invariant solution in metastable equilibrium with $Na_2SO_4 \cdot 10H_2O$ and the double salt.

As already stated the stable range for the double salt at this temperature appears to be extremely short. Because of the close similarity of the slopes of the sodium sulfate and double salt curves, the narrowness of the isothermally invariant area for the ocurrence of both phases together, the slowness with which transformations take place, and the tendency for solutions to remain in metastable equilibrium with either sodium sulfate or double salt separately, the isothermally invariant point for the two solid phases sodium sulfate + double salt is very difficult to obtain at all three temperatures, especially at 25°. At 25° seven complexes gave a solution with the composition 46.62% $NaClO_3$ and 3.87% Na_2SO_4, with sodium chlorate and double salt as solid phases. Two complexes, with sodium chlorate and sodium sulfate apparently as solid phases, gave the same composition, 46.64% $NaClO_3$ and 3.86% Na_2SO_4. The former are probably stable, the latter metastable. Probably the most that can be said with certainty from the data is that the quintuple point representing the disappearance of the double salt as a stable phase (with lowering temperature) must occur at a temperature close to and probably slightly below 25°.

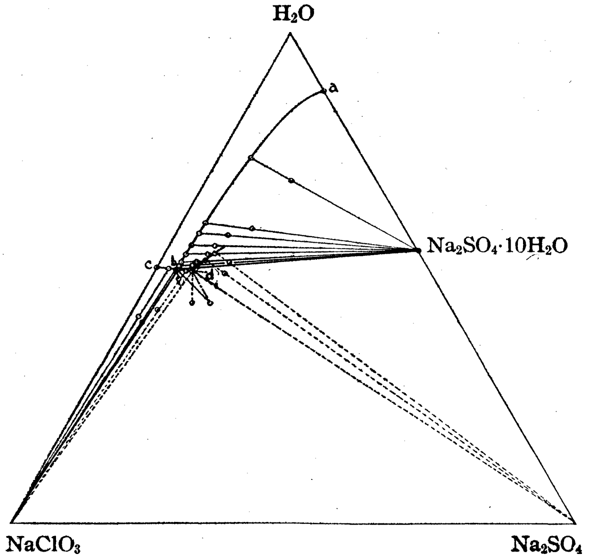

Fig. 5.—15° Isotherm: $NaClO_3$–Na_2SO_4–H_2O.

15° Isotherm.—The only stable solid phases at this temperature are $Na_2SO_4 \cdot 10H_2O$ for the curve a-b, and $NaClO_3$ for b-c. The point d is an isothermally invariant solution in metastable equilibrium with sodium chlorate and anhydrous sodium sulfate; the curve for the solubility of the latter could be followed for only a short distance, being extremely unstable. At this temperature, finally, the double salt is not stable at all; it formed only as a temporary metastable phase a few times, but was too labile in respect to the decahydrate to allow any part of its solubility curve to be determined.

Summary

1. Solubility measurements are given for the system $KClO_3$–K_2SO_4–H_2O at 15, 25 and 45°; no double salt formation is found in this system.

2. The system $NaClO_3$–Na_2SO_4–H_2O has been studied at 15, 25, 45 and 75°. A double salt with the formula $NaClO_3 \cdot 3Na_2SO_4$ is formed at 25° and above, having always a very short range of stable existence, but persisting in metastable equilibrium over a very considerable range of concentration.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Potassium Hydroxide Solutions from Electromotive Force Measurements

BY HERBERT S. HARNED AND MELVIN A. COOK[1]

The electromotive forces of the cell

$$H_2 \mid KOH(m_2) \mid K_xHg \mid KOH(m_1) \mid H_2 \quad (1)$$

have been measured at 25° by Knobel.[2] Following the procedure which Harned and Hecker[3] employed with sodium hydroxide solutions, a thorough investigation of these cells has been made. Measurements have been obtained from 0 to 35° at 5° intervals and at concentrations from 0.1 to 4 *M*. For purposes of theoretical computations, these measurements have been supplemented with density determinations over the above ranges of temperature and concentration. From these data, the activity coefficient, the relative partial molal heat content and the relative partial molal heat capacity of this hydroxide have been computed.

Experimental Results

The method of measurement and cell technique was with slight modification the same as described by Harned,[4] and Harned and Hecker.[3] The hydrogen electrodes were of the usual platinized platinum foil type. The potassium amalgam was prepared as described by Harned and was approximately 0.02% potassium. The temperature control was ±0.02°. A stock solution of 5 *M* potassium hydroxide was made from the highest grade analyzed chemical. The carbonate present was removed by addition of a slight excess of a barium hydroxide solution. The solution was then boiled under vacuum, and kept under an atmosphere of hydrogen. From this solution a reference solution of 0.05 *M* hydroxide was made. The solutions of varying concentrations were made from the 5 *M* stock solution by weight dilution with water. Potassium hydroxide solutions were analyzed by titration with a gravimetrically standardized hydrochloric acid solution. The concentrations were all known to within ±0.05%.

The densities of the solutions were obtained by means of dilatometers in the manner described by Harned, Keston and Donelson.[5]

The measurements of the electromotive forces were made with a Leeds and Northrup Type K potentiometer. Results were obtained at 25 different potassium hydroxide concentrations and at 5° intervals from 0 to 35°. Duplicate or triplicate results were obtained at each concentration and temperature. The results, all of which were reproducible to within ± 0.08 mv., were smoothed to round concentrations by plotting the function $(E - 2k \log m/0.05)$, where k is $2.303\, RT/F$, against the molality. 8.315, $t + 273.1$ and 96,500 were employed for R, T and F, respectively. Since a table of all these results is voluminous, we have resorted to the expediency of expressing the electromotive forces at a given concentration by means of the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \quad (2)$$

The constants of this equation were determined by the graphical method used by Harned and Nims.[6] The values of E_{25}, a and b are given in

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[1] This communication contains part of the material of a dissertation to be presented by Melvin A. Cook to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1937.

[2] Knobel, THIS JOURNAL, **45**, 70 (1923).

[3] Harned and Hecker, *ibid.*, **55**, 4838 (1933).

[4] Harned, *ibid.*, **47**, 677 (1925).

[5] Harned, Keston and Donelson, *ibid.*, **58**, 989 (1936).

[6] Harned and Nims, *ibid.*, **54**, 423 (1932).

Table I. The next to last column of the table gives the average magnitude of the deviation of the observed results and those computed by equation (2) at each of the concentrations. b' are smoothed values of b to be used for the computation of the relative partial molal heat capacity.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: $H_2 \mid KOH(m) \mid K_xHg \mid KOH(0.05) \mid H_2$ at 25° and Constants of Equation (2). Valid from 0 to 35°

m	E_{25}	$a \times 10^6$	$-b \times 10^6$	Δ, mv.	$-b' \times 10^6$
0.1	0.03426	108.5	0.46	0.01	0.56
.15	.05330	167.0	.60	.05	.58
.25	.07834	252.8	.63	.03	.64
.35	.09451	308.8	.69	.04	.70
.5	.11237	345.9	.83	.05	.81
.75	.13423	429.6	1.06	.05	.97
1.0	.15044	494.2	1.17	.05	1.13
1.5	.17538	579.9	1.23	.02	1.43
2.0	.19511	632.9	1.43	.05	1.74
2.5	.21219	680.7	1.86	.06	2.02
3.0	.22759	699.3	2.54	.07	2.30
3.5	.24240	725.0	2.73	.10	2.65
4.0	.25556	746.0	2.80	.07	2.78

The density data have been expressed by an equation of the form

$$d = d_0 + a'm + b'm^{3/2} \qquad (3)^7$$

where d_0 is the density of water at the temperature in question and a' and b' are constants. The latter were evaluated from the observed densities by the method of least squares. Values of the constants of equation (3) are listed in Table II.

TABLE II

DENSITY DATA: CONSTANTS OF EQUATION (3)

t	d_0	a'	b'
0	0.9999	0.05875	0.00667
5	1.0000	.0572	.0065
10	0.9997	.05555	.0058
15	.9991	.0548	.0055
20	.9982	.0535	.0051
25	.9970	.0526	.0047
30	.9957	.0514	.0043
35	.9940	.0516	.0045

Activity Coefficients

Upon rearranging the usual expression for the electromotive force for cells of the type used here, we obtain

$$\log \frac{\gamma}{\gamma_{0.05}} = \frac{E}{2k} - \log \frac{m}{0.05} - {}^1/_2 \log \frac{p_{0.05}}{p} \qquad (4)$$

Here γ is the activity coefficient of the hydroxide, $\sqrt{\gamma_K \gamma_{OH}}$, at a concentration m, $\gamma_{0.05}$ the value of this quantity at the reference concentration, 0.05 M, $p_{0.05}$ the vapor pressure of the reference solution and p the vapor pressure of the solution of hydroxide at the concentration m.

The Gibbs–Duhem equation may be converted to the form

$$-\mathrm{d} \log p = \frac{2}{55.51 \times 2.303}\, \mathrm{d}m + \frac{2}{55.51}\, m\, \mathrm{d} \log \gamma \qquad (5)$$

since $\log \gamma_{0.05}$ is a constant, $\mathrm{d} \log \gamma$ in the last term may be written $\mathrm{d} \log \gamma/\gamma_{0.05}$. Making this substitution in equation (5) and integrating, we obtain

$${}^1/_2 \log \frac{p_{0.05}}{p} = \frac{1}{55.51} \int_{0.05}^{m} m\, \mathrm{d} \log \frac{\gamma}{\gamma_{0.05}} + \frac{m - 0.05}{55.51 \times 2.303} \qquad (6)^8$$

To evaluate the first term on the right of equation (6), values of $\log \gamma/\gamma_{0.05}$, obtained from equation (4) (omitting the last term), are plotted against m, and the area under the curve evaluated. Upon substituting this result in equation (6), 1/2 $\log p_{0.05}/p$ is obtained. This result is substituted in equation (4) and a more exact value of $\log \gamma/\gamma_{0.05}$ is obtained. This result is employed to reëvaluate the first term on the right of equation (6). This method of arithmetical approximation is repeated until both equations (4) and (6) are satisfied. In Table III, values of 1/2 $\log p_{0.05}/p$ are given. This quantity changes at the most only about 3 units in the fourth decimal place between the limits 0 and 35°. Since 1 in this decimal place corresponds to a difference of 0.01 mv. in the electromotive force, an assumption of constancy is within the error of the experiment.

TABLE III

VALUES OF THE VAPOR PRESSURE TERM

m	0.1	0.15	0.25	0.35	0.5	0.75	
${}^1/_2 \log p_{0.05}/p$	.0004	.0008	.0015	.0022	.0033	.0053	
m	1.0	1.5	2.0	2.5	3.0	3.5	4.0
${}^1/_2 \log p_{0.05}/p$	0.0072	0.0106	0.0154	0.0210	0.0278	0.0344	0.0412

By substitution of these values for the vapor pressure correction in equation (4), values of $\log \gamma/\gamma_{0.05}$ were obtained. For purposes of extrapolation, we have employed the equation of Debye and Hückel which for a 1–1 electrolyte is

$$\log \gamma = -uc^{1/2}/(1 + A(2c)^{1/2}) + Bc - \log(1 + 0.036m) \qquad (7)$$

For the activity coefficient ratio, this equation becomes

$$\log \gamma/\gamma_{0.05} = -u[c^{1/2}/(1 + A(2c)^{1/2}) - (0.05)^{1/2}/(1 + A(0.1)^{1/2})] + B(c - 0.05) - \log(1 + 0.036m)/(1 + 0.0018) \qquad (8)$$

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(7) Root, THIS JOURNAL, 55, 850 (1933).

(8) Harned and Hecker's[3] equation (5) due to typographical error differs from this equation.

TABLE IV

ACTIVITY COEFFICIENTS OF POTASSIUM HYDROXIDE

m	0°	10°	20°	25°	35°
0.05	(0.829)	(0.828)	(0.825)	(0.824)	(0.822)
.1	.795 (0)	.798 (−2)	.798 (0)	.798 (0)	.793 (2)
.15	.778 (0)	.778 (0)	.776 (0)	.774 (1)	.771 (0)
.25	.758 (−2)	.759 (−2)	.757 (−1)	.757 (−1)	.751 (3)
.35	.738 (0)	.740 (0)	.739 (−2)	.739 (−2)	.733 (0)
.5	.737 (−2)	.735 (1)	.732 (2)	.728 (4)	.724 (3)
.75	.742 (−2)	.743 (−1)	.741 (0)	.740 (1)	.733 (4)
1.0	.755 (0)	.758 (0)	.756 (3)	.756 (2)	.752 (2)
1.5	.809	.815	.814	.814	.809
2.0	.889	.890	.889	.888	.879
2.5	.974	.981	.980	.974	.965
3.0	1.088	1.094	1.087	1.081	1.065
3.5	1.219	1.231	1.219	1.215	1.195
4.0	1.391	1.389	1.361	1.352	1.314
u	0.487	0.494	0.502	0.506	0.516
K'	.2295	.2305	.2317	.2324	.2340
B	.118	.125	.128	.130	.132

(1). $a = 3.7$ Ångström units.

(2). The number in ( ) is the difference in the third decimal place between the observed γ and the value calculated by equation (7), it being positive when the calculated value is greater than the observed.

which is suitable for evaluating A and B. By using values of c computed from the equation

$$c = [1000m/(1000 + 56.1m)](d_0 + a'm + b'm^{3/2}) \quad (9)$$

the constants A and B may be determined by means of equation (8) from two values of the activity coefficient ratio. Firstly, the 0.1 and 1 M results were employed, and secondly, the 0.25 and 0.5 M were used at each temperature. Both computations gave consistent results.

The apparent ionic diameter, a, in Ångström units was obtained from D by means of the equation derived from theory

$$A = K'a \quad (10)$$

by using values of K' computed by Harned and Ehlers.[9] No indication of a variation of this quantity with temperature was found. The results of the calculation indicated a constant value of 3.7 Å.

The values of the constant B may be expressed within narrow limits by the equation

$$B = 0.118 + 0.00072t - 1.06 \times 10^{-5}t^2 \quad (11)$$

The observed activity coefficients at some of the temperatures are given in Table IV. The differences between these values and those computed by equation (7) are designated in the table. Values of the parameters of equation (7) necessary for this computation are given in the bottom rows of the table. The range of validity of equation (7) is from 0 to 1 M.

The Relative Partial Molal Heat Content

$\overline{L}_2$ was evaluated at concentrations from 0.05 to 1 M by the differentiated form of equation (7). If the value of ln γ given by equation (7) be substituted in the equation for $\overline{L}_2$, namely

$$\overline{L}_2 = -\nu RT^2\, \partial \ln \gamma/\partial T \quad (12)$$

and the differentiation performed, we obtain

$$\overline{L}_2 = U'c^{1/2}/(1 + A(2c)^{1/2}) - V'/(1 + A(2c)^{1/2})^2 (c\mathrm{d}A/\mathrm{d}T + A\ \mathrm{d}c/2\mathrm{d}T) + W'(B\mathrm{d}c/\mathrm{d}T + c\mathrm{d}B/\mathrm{d}T) \quad (13)$$

where U', V' and W' are isothermal constants[5] (eq. 11, Table VI) derived from theory. $\mathrm{d}B/\mathrm{d}T$ was obtained by differentiating equation (11). $\mathrm{d}A/\mathrm{d}T = a\ \mathrm{d}K'/\mathrm{d}T$ was obtained graphically from the values of K' in Table IV. Since equation (9) may be written $c = A'm + B'm^2 + C'm^{5/2}$, we have that

$$\mathrm{d}c/\mathrm{d}T = m\mathrm{d}A'/\mathrm{d}T + m^2\mathrm{d}B'/\mathrm{d}T + m^{5/2}\mathrm{d}C'/\mathrm{d}T \quad (14)$$

The values of these differential coefficients were determined graphically at each temperature and then used to determine $\mathrm{d}c/\mathrm{d}T$. All the required quantities were then substituted in equation (13) and values of $\overline{L}_2$ at concentrations up to 1 M were obtained.

In addition to this calculation, the partial molal heat content relative to the 0.05 M solution was computed by the Gibbs–Helmholtz equation

$$\overline{H}_m - \overline{H}_{0.05} = NE'F - NF\mathrm{d}E'/\mathrm{d}T \quad (15)$$

in which E' is the electromotive force corrected for the vapor pressure term. Since we have

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[9] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933). The values of u used were also taken from this paper.

shown that this term does not vary sufficiently with the temperature to affect our results, the equation for E' is according to equation (2) simply

$$E' = E'_{25} + a(t - 25) + b(t - 25)^2 \qquad (16)$$

whence

$$\overline{H}_m - \overline{H}_{0.05} = NE'F - NFT[a + 2b(t - 25)] \qquad (17)$$

The values of this quantity obtained by this method were within 20 calories of those computed by equation (13) except in the range of concentration of 0.1 to 0.25 M at temperatures below 15° where a discrepancy of the order of 50 calories sometimes occurred. We consider that in these cases the computation by equation (13) is the more reliable. At concentrations from 1.5 to 4 M, inclusive, equation (17) was employed. These results are given within 10 cal., which is less than the error in their determination, by the equation

$$\overline{L}_2 = \overline{L}_2^0 + \alpha t + \beta t^2 \qquad (18)$$

where $\overline{L}_2^0$ is the value of $\overline{L}_2$ at 0°, and α and β are constants. Table V contains the values of these constants at the designated hydroxide concentrations. A plot of these results is shown in Fig. 1.

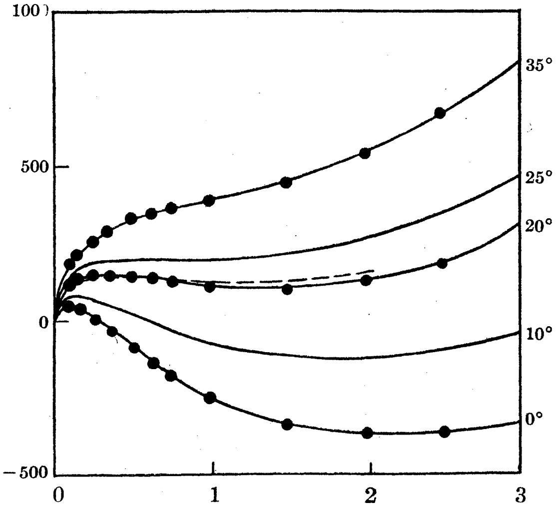

Fig. 1.—The relative partial molal heat content (Rossini's values at 18° are represented by the dotted line).

Rossini[10] has computed $\overline{L}_2$ for potassium hydroxide in aqueous solution at 18° from heat of dilution data. These values are also plotted in the figure whence it is apparent that excellent agreement is obtained in the concentration range from 0.05 to 1 M. At concentrations from 1 to 2 M, the agreement is not so good.

TABLE V

RELATIVE PARTIAL MOLAL HEAT CONTENT AND SPECIFIC HEAT-CONSTANTS OF EQUATION (18) AND (19)

m	α	β	$\overline{L}_2^0$	$(\overline{C}_{p_2} - \overline{C}_{p_2}^0)_{25}$
0.05	2.4	0.017	37	3.2
.1	3.6	.029	41	5.0
.15	4.7	.030	30	6.2
.25	6.4	.032	− 1	8.0
.35	8.2	.034	− 35	9.9
.5	10.4	.036	− 95	12.2
.75	13.6	.040	−180	15.6
1.0	16.2	.043	−270	18.4
1.5	20.6	.050	−335	23.1
2.0	24.6	.057	−381	27.4
2.5	28.2	.063	−390	31.3
3.0	31.5	.070	−356	35.0
3.5	34.5	.078	−335	38.4
4.0	37.4	.081	−226	41.5

The Relative Partial Molal Heat Capacity

By differentiation of $\overline{L}_2$ with respect to the temperature, $(\overline{C}_{p_2} - \overline{C}_{p_2}^0)$ is found to be expressed by

$$(\overline{C}_{p_2} - \overline{C}_{p_2}^0) = \alpha + 2\beta t \qquad (19)$$

Values of this quantity at 25° are given in the last column of Table V. In Fig. 2, these results have been plotted against $m^{1/2}$ and are designated by circles. The two solid straight lines represent the equations which Gucker and Schminke[11] and Rossini[12] proposed to express the results obtained from calorimetric data. The limiting slope of the Debye and Hückel theory is also represented. The maximum difference between our results and those of Gucker and Sch-

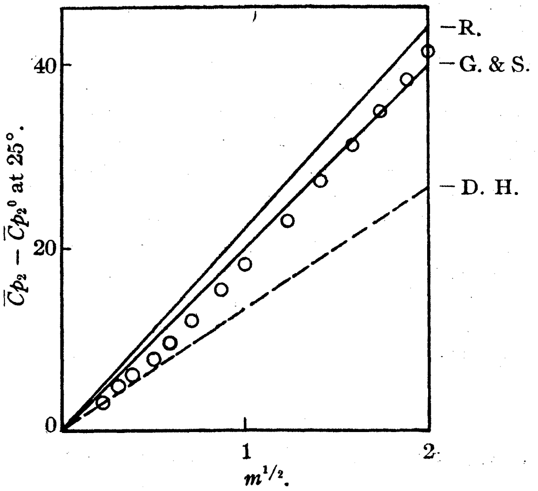

Fig. 2.—The relative partial molal heat capacity; R. Rossini; G. & S., Gucker and Schminke; D. H., Debye–Hückel limiting law.

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[10] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

[11] Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932).

[12] Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

minke is two calories. This is good agreement considering all the difficulties encountered in this determination. Our results indicate a slight curvature.

Summary

Measurements of the electromotive forces of the cell $H_2 \mid KOH(m) \mid K_xHg \mid KOH(0.05) \mid H_2$ have been made from 0 to 35° inclusive at 5° intervals and m was varied from 0.1 to 4 M.

2. From these data, the activity coefficient, relative partial molal heat content, and the relative partial molal heat capacity have been computed. Satisfactory agreement with similar results derived from calorimetric data has been obtained.

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

The Heat Capacity of Carbon Disulfide from 15 to 300°K. The Entropy and Heat of Fusion of Carbon Disulfide

BY OLIVER L. I. BROWN[1] AND GEORGE G. MANOV

The heat capacity of solid and liquid carbon disulfide, and the heat of fusion have been determined in order to complete the data necessary for the calculation of the entropy of carbon disulfide.

Material.—The carbon disulfide was fractionally distilled several times after drying with calcium chloride. About two liters of material obtained in this way was fractionally distilled using a special column about 60 cm. high, packed with brass shoe eyelets. The distilling flask contained phosphorus pentoxide to remove the last traces of water, and the distillation was carried out in an atmosphere of helium gas to avoid possible oxidation of the carbon disulfide. About half the distillate was collected as a middle fraction, which served as the starting material for a new fractionation. This procedure was repeated a third time before the product was placed in the calorimeter. The calorimeter, which was copper, was filled in such a manner that the carbon disulfide came in contact with only helium, copper, glass and the solder used for sealing the top. A small amount of helium was admitted to ensure heat conduction in the sample before the calorimeter was sealed. From the change in melting point with percentage

TABLE I

HEAT CAPACITY OF CARBON DISULFIDE; 0°C. = 273.1°K.

Run	T, °K.	C_p cal./mole/deg.	ΔT
37	15.05	1.65	2.771
38	17.50	2.22	2.239
39	20.15	2.87	3.113
40	23.06	3.48	2.754
41	26.19	4.18	3.237
42	29.76	4.96	3.953
43	33.68	5.64	3.970
44	37.67	6.32	4.054
45	42.22	6.97	4.676
46	47.39	7.53	5.670
47	52.25	7.91	4.646
48	57.52	8.50	5.884
49	63.47	8.92	6.289
50	69.96	9.36	6.856
51	75.54	9.57	4.579
52	81.19	9.86	6.543
53	87.21	10.31	6.496
5	89.37	10.31	4.584
6	94.17	10.61	4.733
54	94.21	10.76	6.441
7	99.00	10.98	4.950
8	104.00	11.31	4.708
1	108.17	11.48	3.937
9	108.93	11.59	5.114
10	114.03	11.82	5.854
2	119.36	12.04	4.013
11	119.91	12.07	5.913
12	126.03	12.39	5.397
13	131.54	12.58	5.578
14	137.38	12.81	6.112
15	144.31	13.05	6.521
16	150.47	13.26	5.747
3	152.23	13.34	4.720
17	155.63	13.50	4.548
4	156.83	13.53	4.488
18	158.74	14.46	1.621
	161.11	Melting point	
19	163.93	18.10	4.895
20	169.51	17.97	6.314
21	176.17	17.91	6.968
22	183.04	17.94	6.672
23	189.64	17.99	6.418
24	192.30	17.91	5.926
25	198.44	17.90	6.446
26	205.28	18.00	7.007
27	211.83	18.02	5.884
28	219.31	17.95	7.620
29	227.34	17.93	8.347
30	235.80	18.00	7.764
31	244.25	18.00	8.712
32	253.06	17.88	8.430
33	261.66	18.10	8.034
34	269.69	18.08	7.478
35	278.22	18.06	8.932
36	297.43	18.17	9.440

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melted and the absence of appreciable premelting, it was estimated that the solid-insoluble liquid-soluble impurity was less than 0.001 mole per cent. Measurements were made on a sample of 145.987 g. (weight *in vacuo*).

Heat Capacity Measurements.—The method used for the heat capacity measurements has been described previously.[2] One calorie was taken equal to 4.1833 international joules, and the molecular weight of carbon disulfide was taken as 76.12. The heat capacities are tabulated in Table I, and plotted as a function of temperature in Fig. 1. The values of the heat capacities are listed in the order of increasing temperature, but are numbered in the order in which they were determined. No previous values for the heat capacity of solid carbon disulfide have been reported in the literature. Previous measurements on the liquid have been made by Koref,[3] Hartung[4] and Battelli.[5] Koref made seven determinations, all of which agree with our results to within 0.2%. Hartung reported only one value, which agrees with our results to within 0.16%. Our results are not in agreement with those of Battelli, whose values differ in some cases by as much as 17% from those reported here.

Melting Point and Heat of Fusion.—The melting point and heat of fusion were obtained by the method described by Johnston and Giauque.[6] The melting point determination is summarized in Table II. The resistance thermometer had a temperature coefficient of one ohm per degree in this range. The values of the resistance are included in the table because of the greater accuracy of the resistance thermometer for small temperature changes, although the actual temperatures were obtained from the thermocouple readings. The thermocouple was calibrated in terms of the laboratory standard No. 17, and is believed to be accurate to 0.05 °K. After the completion of these measurements the thermocouple was compared directly with the boiling point of hydrogen and found to correspond to within 0.02 °K.

Previous values for the melting point have been reported by Henning[7] (−112.00°C.), Timmermans, van der Horst and Onnes[8] (−111.6°C.), Timmermans[9] (−111.8°C.), Keyes, Townshend and Young[10] (−112.97°C.), and Skau[11] (−111.88°C.).

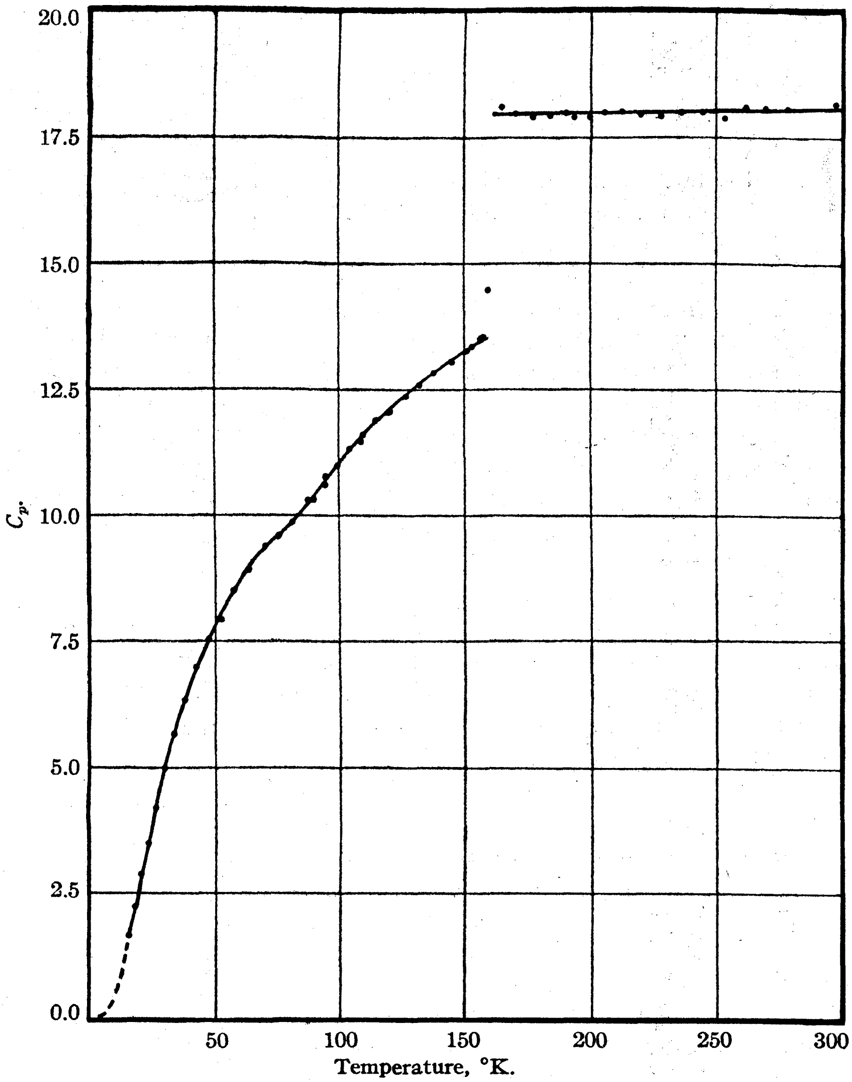

Fig. 1.—Molal heat capacity of carbon disulfide.

The heat of fusion of carbon disulfide was found to be 1049.0 cal. per mole. We were able to make only one heat of fusion measurement, as the calorimeter unfortunately split open after the completion of run No. 54, and while the calorimeter was being heated up to the melting point in order to make a second determina-

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(2) Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928).

(3) Koref, *Ann. Physik*, **36**, 49 (1922).

(4) Hartung, *Trans. Faraday Soc.*, **11**, 64 (1915).

(5) Battelli, *Atti accad. Lincei*, **16**, I, 243 (1907).

(6) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

(7) Henning, *Ann. Physik*, **43**, 282 (1914).

(8) Timmermans, van der Horst and Onnes, *Compt. rend.*, **174**, 365 (1922).

(9) Timmermans, *Comm. Phys. Lab. Leiden*, *Suppl.* *No.* **64**, 3 (1929).

(10) Keyes, Townshend and Young, *J. Math. Phys.*, Mass. Inst. Tech., **1**, 243 (1922).

(11) Skau, *J. Phys. Chem.*, **37**, 609 (1933).

TABLE II

MELTING POINT OF CARBON DISULFIDE

Date	Time	Resistance thermometer, ohms	T, °K.	% melted
7/20/35	3:00 p.m.	(Heated into melting point)		
	5:50 p.m.	151.3615	161.113	10
	7:10 p.m.	151.3610	161.118	10
7/21/35	12:45 a.m.	151.3611	161.114	30
	11:00 a.m.	151.3596	161.122	55
	2:00 p.m.	151.3606	161.101	70
	3:30 p.m.	151.3623	161.099	70

Average melting point 161.11 ± 0.05°K. (−111.99°C.).

tion of the heat of fusion. Since circumstances have arisen which make it unlikely that we will repeat these measurements, we have considered it best to offer our results even though the lack of a second heat of fusion makes it difficult to estimate the total probable error. We have no reason to suspect the accuracy of our single measurement, and in similar measurements made in this Laboratory by other workers the error has not usually exceeded 0.3% or about 3 cal. per mole. We have assigned the total probable error in the entropy as 0.5 E. U., which we believe to be a very conservative figure.

The heat of fusion of carbon disulfide has been determined indirectly by Timmermans,[12] and Mitsukuri and Aoki,[13] who measured the change in freezing point when organic solutes were dissolved in carbon disulfide. The former gives 1350 cal. per mole with an uncertainty of 10 to 20%, and the latter give 660 cal. per mole for the heat of fusion.

Entropy of Carbon Disulfide.—The entropy calculations are summarized in Table III. The graphical portion of the entropy was obtained from an integration of C_p *vs.* log T, and also as an arithmetical check, from an integration of C_p/T *vs.* T. The entropy of vaporization was taken from the work of Mathews,[14] who found by direct vaporization using electrical energy that the heat of vaporization of carbon disulfide at 45.29° was 84.07 ± 0.03 cal. per gram. The vapor pressure, heat capacity of the vapor, critical temperature and critical pressure used in calculating the last three items in Table III were taken from the "International Critical Tables."[15]

TABLE III

CALORIMETRIC ENTROPY OF CARBON DISULFIDE

0–15.05°K., Debye extrapolation	0.629 E. U.
15.05–161.11°K., solid, graphical	17.881
Fusion, 1049.0/161.11	6.511
161.11–298.1°K., liquid, graphical	11.080
298.1–318.39°K., liquid, extrapolated	1.192
Vaporization, 84.07 × 76.12/318.39	20.099
Compression, $R \ln (736.5/760)$	−0.063
318.39–319.35°K., vapor	.036
Berthelot ideal gas correction	.110

Entropy of ideal gas at 319.35°K., 57.48 ± 0.5

The entropy of gaseous carbon disulfide may be calculated from spectroscopic data using the moment of inertia of Cross,[16] which was checked by Sanderson,[17] the vibration frequencies of Dennison and Wright[18] and the methods of Giauque.[19] The result of this calculation at the temperature of the normal boiling point, 319.35°K., is summarized in Table IV.

TABLE IV

ENTROPY OF CARBON DISULFIDE FROM SPECTROSCOPIC DATA

$S°$ Rotation		15.725 E.U.
$S°$ Translation		39.255
$S°$ Vibration	v_1 = 655.5 cm.$^{-1}$	0.441
	v_2 = 396.8 (double wt.)	2.167
	v_3 = 1532	0.016
$S_{319.35}$; CS_2 (gas)		57.60

The calorimetric value (57.48 E. U.) agrees with the spectroscopic value (57.60 E. U.) well within the estimated experimental error.

Summary

The heat capacity and heat of fusion of carbon disulfide have been measured. The entropy calculated from calorimetric data agrees with the spectroscopic value within the experimental error. The entropy of liquid carbon disulfide at 298.1°K. was found to be 36.10 E. U.

BERKELEY, CALIF. RECEIVED JANUARY 18, 1937

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(12) Timmermans, *Bull. soc. chim. Belg.*, **43**, 626 (1934).

(13) Mitsukuri and Aoki, *Sci. Rep. Tôhoku Imp. Univ.*, **15**, 61 (1926).

(14) Mathews, THIS JOURNAL, **48**, 562 (1926).

(15) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926.

(16) Cross, *J. Chem. Phys.*, **3**, 821 (1935).

(17) Sanderson, *Phys. Rev.*, **50**, 209 (1936).

(18) Dennison and Wright, *ibid.*, **38**, 2077 (1931).

(19) Giauque, THIS JOURNAL, **52**, 4808 (1930).

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. III. Potassium Chloride. IV. Calcium Chloride

BY THEODORE SHEDLOVSKY AND DUNCAN A. MACINNES

In the two previous papers in this series[1,2] it was shown that accurate activity coefficients can be obtained from the results of potential measurements on concentration cells with transference of the form

$$\text{Ag; AgCl, MCl}\,(C_1)\text{:MCl}(C_2)\text{, AgCl; Ag} \qquad \text{(A)}$$

in which M represents a positive ion constituent. The computations involved the use of the equation

$$-E = \frac{2RT}{F}\int_{C_1}^{C_2} t \,\mathrm{d}\log Cf \qquad (1)$$

in which E is the potential of a cell of type A, t is the transference number of the positive ion, C is the concentration in gram moles per liter of solution and f the activity coefficient. The papers mentioned describe the determination of the activity coefficients of sodium chloride and of hydrochloric acid, respectively, up to concentrations of 0.1 normal, the upper limit being determined by the available accurate transference data. We have continued the measurements to include solutions of potassium chloride and calcium chloride. The first of these was chosen because it is a commonly used type and reference salt, and also because precise determinations of the transference numbers of potassium chloride have been made over a wide range of concentrations. Longsworth[3] has obtained transference data for that substance over the concentration range 0.001 to 1.0 N, by the moving boundary method, and MacInnes and Dole[4] have used the Hittorf method over the range 0.2 to 3.0 N. The two methods gave closely agreeing values, the greater precision, however, being obtained with the moving boundary method.

Calcium chloride has been added to the series because it is an example of a salt of a higher valence type. For a bi-univalent electrolyte equation (1) must be modified to

$$-E = \frac{3RT}{2F}\int_{C_1}^{C_2} t \,\mathrm{d}\log Cf \qquad (2)$$

The value of the coefficient 3/2 may be explained readily by the fact that the passage of 2 faradays of current through a calcium chloride concentration cell "without transference" is accompanied by the transport of three gram moles of ions, *i. e.*, one of calcium and two of chloride. Accurate transference numbers for calcium chloride have been obtained recently by Longsworth[5] in the concentration range C = 0.005 to 0.1 N.

The experimental procedure employed in determining the potentials of the concentration cells followed closely that described for cells containing hydrochloric acid.[2] The potassium chloride was of the best obtainable grade, and was given a further purification by precipitation with hydrogen chloride gas, and repeated crystallization from conductivity water. The calcium chloride was from the same sample as was used by Shedlovsky and Brown[6] in their conductance measurements. The solutions were made up by weight dilution from known stock solutions and their concentrations confirmed by accurate conductance determinations.[6,7] The two silver–silver chloride electrodes in the concentration cell never differed from each other by more than 0.02 mv. and the effect of this small difference of potential was eliminated, within a few microvolts, by duplicate measurements with the positions of the two solutions in the cell reversed. From the experimental data values of activity coefficient ratios have been computed by the method described in the first paper of this series.[8]

Activity coefficients may be stated in terms of concentrations, C (moles per liter), m (moles per 1000 g. of solvent), mole fractions, n and other concentration scales which will not concern us here. They are connected by the relation

$$a_c : a_m : a_n = fC : \gamma m : f_r n \qquad (3)$$

in which a_c, a_m and a_n are activities on the scale represented by the subscripts, and f, γ and f_r

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[1] Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

[2] Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936).

[3] Longsworth, *ibid.*, **54**, 2741 (1932); MacInnes and Longsworth, *Chem. Rev.*, **11**, 210 (1932).

[4] MacInnes and Dole, THIS JOURNAL, **53**, 1357 (1931).

[5] Longsworth, *ibid.*, **57**, 1185 (1935).

[6] Shedlovsky and Brown, *ibid.*, **56**, 1066 (1934).

[7] Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

[8] In that paper,[1] equation (11) should read

$$-\Delta\log f = -\frac{E}{118.29\,t_1} - (\log C_2 - \log C_1) - \frac{1}{t_1}\int^{2} \Delta t \,\mathrm{d}\log C + \frac{1}{t_1}\int_{1}^{2} \Delta t \,\mathrm{d}(\Delta\log f)$$

are the corresponding activity coefficients. Since it is assumed that these activity coefficients approach unity at infinite dilution they are measures of deviations from ideal solutions defined in three different ways. The activity coefficient f_r has been called "rational" because it measures departures from Raoult's law.[9] The relations between f, γ and f_r are the following

$$f_r = f(d - 0.001MC + 0.018\nu C)/d_0 = \gamma(1 + 0.018\nu m) \quad (4)$$

in which ν is the number of ions into which the solute dissociates, M is the molecular weight of the solute and d and d_0 are the densities of the solution and solvent.

To obtain the activity coefficients, f, from values of $-\Delta\log f$ computed directly from the data it was necessary to evaluate the activity coefficient of the reference solution. To this end use was made of the Debye–Hückel equation in the form

$$-\log f = \Delta\log f - A = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) + \log\frac{(d - 0.001MC + 0.018\nu C)}{d_0} \quad (5)$$

in which α is 0.5056 for a uni-univalent and 1.7515 for a bi-univalent electrolyte, respectively, at 25° and β involves the distance of closest approach of the ions. The last term of this equation is of negligible magnitude in dilute solutions.[10] To obtain a value of A a plot was made of $(\Delta\log f - \alpha\sqrt{C})$ against $(A - \Delta\log f)\sqrt{C}$, and the value of A adjusted until it agreed with the intercept of the plot, as described in more detail in the previous papers. With this value of A, $\log f$ values may be obtained directly from $\Delta\log f$, as indicated in equation (5).

Results and Discussion

(a) Potassium Chloride.—The results of the series of measurements on the potentials of potassium chloride concentration cells are given in Table I. The first column of the table contains the concentrations C_2 in moles per liter at 25°. The reference solution C_1 was 0.1 mole per liter. The second and third columns contain the corresponding potentials, E, in millivolts, and the transference numbers, t. The fourth column lists values of $-\Delta\log f$. From these figures the activity coefficients f, given in the next column, were obtained with the aid of the value of A determined as described above. The value of β in equation (5) was found to be 1.350, corresponding to a distance of closest approach of 4.13 Å.[11] Using this constant and equation (5), the activity coefficients "f computed" in column 6 were calculated. It will be seen that the agreement between the experimental and computed activity coefficients extends to about $C = 0.2$. This concentration is considerably higher than the usual upper limit of validity of this equation. In the cases of sodium chloride and hydrochloric acid it is about $C = 0.04$.

For higher concentrations Hückel[9] has proposed the equation

$$-\log f_r = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) - DC \quad (6)$$

in which D is a constant. A careful analysis, to be published elsewhere, has proved that an equation of this type will not fit our data above $C = 0.5$. However, the equation

$$-\log f = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) - DC\log C + \log[(d - 0.0386C)/d_0] \quad (7)$$

was found to agree surprisingly closely with the experimental results throughout the concentration range studied, *i. e.*, $C = 0.005$ to 3.0, as can be seen by comparing the figures in columns 5 and 7 of Table I. The values of β and D in this equation were found to be 1.50 and 0.0365, respectively.

It has, however, been usual to express activity coefficients in terms of γ values, *i. e.*, a_m/m, in which m represents moles per 1000 g. of water. The relation between f and γ is given in equation (4). Thus, equation (7), which was obtained from the data in Table I, can also be put in the form

$$-\log\gamma = \frac{0.5056\sqrt{C}}{1 + 1.50\sqrt{C}} - 0.0365C\log C + \log(1 + 0.036m) \quad (7a)$$

For reference, values of γ at round concentrations for potassium chloride at 25° are given in Table II.

(b) Calcium Chloride.—The results of measurements and computations on solutions of calcium chloride are given in Table III, which is

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(9) Hückel, *Physik. Z.*, **26**, 93 (1925).

(10) In the previous papers of this series this term was not included. For sodium chloride and hydrochloric acid it is negligible, within the experimental error, up to $C = 0.1$, the upper limit of the measurements.

(11) The last term in equation (5) was computed with the aid of the relation

$$d = 0.99707 + 0.04805C - 0.00230C^{3/2}$$

for the density, d, at 25°, of potassium chloride solutions, from the data given in the "International Critical Tables." For the density, d, at 25°, of calcium chloride solutions the corresponding equation is

$$d = 0.99707 + 0.0924C - 0.0042C^{3/2}$$

from the measurements of Shedlovsky and Brown.[6]

TABLE I

THE POTENTIALS OF THE CONCENTRATION CELL: Ag; AgCl, KCl (0.1): KCl (C_2), AgCl; Ag AT 25° AND THE COMPUTATION OF THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION

Concn. moles per liter at 25°, C_2	E. m. f. mv., E	Trans. no., t	Log activity coeff. ratio, $-\Delta \log f$	Activity coefficients f exptl.	f, computed equation (5)	f, computed equation (7)
0.0050080	70.765	0.4904	0.0797	0.9273	0.9276	0.9273
.010003	54.025	.4903	.0679	.9024	.9024	.9022
.010053	53.895	.4903	.0679	.9024	.9023	.9022
.020002	37.489	.4901	.0521	.8702	.8701	.8704
.020003	37.483	.4901	.0521	.8702	.8701	.8704
.030000	27.890	.4900	.0416	.8494	.8490	.8497
.030285	27.688	.4900	.0410	.8482	.8485	.8493
.040000	21.170	.4899	.0326	.8320	.8321	.8318
.050106	15.905	.4899	.0256	.8187	.8183	.8179
.059995	11.731	.4899	.0194	.8071	.8067	.8062
.080004	5.113	.4898	.0086	.7872	.7874	.7872
.10000	0.000	.4898	.0000	.7718	.7719	.7720
.20000	−15.757	.4894	− .0289	.7221	.7216	.7226
.50000	−36.453	.4888	− .0692	.6581	.6537	.6594
.9974	−52.442	.4882	− .0924	.6239	.6051	.6234
1.0000	−52.508	.4882	− .0923	.6238	.6049	.6233
3.0000	−80.417	.4857	− .0856	.6337	.5376	.6333

TABLE II

ACTIVITY COEFFICIENTS, γ, AT ROUND MOLAL CONCENTRATIONS FOR POTASSIUM CHLORIDE AT 25°

m = moles/1000 g. H_2O in vacuum	C = moles/liter	$\gamma_{\text{comp.}}$
0.005	0.004985	0.9275
.01	.009968	.9021
.05	.04979	.8172
.10	.09943	.7701
.20	.19830	.7191
.50	.4916	.6516
1.00	.9692	.6069
2.00	1.8827	.5781
3.00	2.7419	.5741
3.55	3.1526	.5765
4.00	3.5514	.5806

TABLE III

THE POTENTIALS OF THE CONCENTRATION CELL: Ag; AgCl, $CaCl_2$ (0.05): $CaCl_2$ (C_2), AgCl; Ag AT 25° AND THE COMPUTATION OF THE ACTIVITY COEFFICIENTS OF CALCIUM CHLORIDE IN AQUEOUS SOLUTION

Concn. moles per liter at 25°, C_2	E. m. f. mv., E	Trans. no., t	Log activity coeff. ratio, $-\Delta\log f$	Activity coefficients f exptl.	f computed equation (5)	f computed equation (8)
0.0018153	47.545	0.4310	0.1679	0.8588	0.8586	0.8586
.0060915	29.263	.4254	.1230	.7745	.7746	.7743
.0095837	22.697	.4224	.1009	.7361	.7364	.7361
.024167	9.751	.4143	.0479	.6514	.6510	.6513
.037526	3.819	.4096	.0191	.6097	.6085	.6099
.050000	0.000	.4060	.0000	.5834	.5810	.5836
.096540	− 8.607	.3958	− .0438	.5275	.5198	.5276

mostly self-explanatory. For this salt the reference concentration was C_1 = 0.05 mole per liter and the computation yielded the value for β of 2.98. This value for β corresponds to a distance of closest approach of 5.27 Å. The sixth column of the table gives values of f computed, using these constants and the appropriate value of α in equation (5). It will be seen that the observed and computed values of the activity coefficient f agree to C = 0.03. It is of great interest to find that the Debye–Hückel theory in its simple form holds for this "unsymmetrical" type of electrolyte. The distance of closest approach is large enough so that the higher terms of the theory[12] are negligible. Agreement between the observed and computed values is observed throughout the range of the measurements with the equation

$$-\log f = \frac{1.7515\sqrt{C}}{1 + 2.814\sqrt{C}} - 0.147C + \log(1.0029d - 0.057C) \quad (8)$$

as can be seen by comparing the fifth and seventh columns of Table III. Values of γ for solutions of calcium chloride at 25° can be obtained from the equation

$$-\log \gamma = \frac{1.7515\sqrt{C}}{1 + 2.814\sqrt{C}} - 0.147C + \log(1 + 0.054m) \quad (8a)$$

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[12] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

Summary

The activity coefficients in aqueous solution at 25° of potassium chloride from $C = 0.005$ to 3.00 moles per liter, and of calcium chloride from $C = 0.002$ to 0.1 have been determined from measurements of potentials of concentration cells with transference, and accurate transference numbers.

It has been found that the simple Debye–Hückel equation $-\log f_r = \alpha \sqrt{C}/(1 + \beta \sqrt{C})$ fits the data, with high precision to $C = 0.2$ for potassium chloride and to $C = 0.03$ for calcium chloride, with distances of closest approach of 4.1 and 5.2Å., respectively.

The equation

$$-\log f_r = \frac{0.5056 \sqrt{C}}{1 + 1.50 \sqrt{C}} - 0.0365C \log C$$

holds for potassium chloride up to $C = 3.00$, and the expression

$$-\log f_r = \frac{1.7515 \sqrt{C}}{1 + 2.814 \sqrt{C}} - 0.147C$$

fits the data for calcium chloride up to $C = 0.1$.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A Revision of the Atomic Weight of Carbon. II

BY GREGORY P. BAXTER AND ARTHUR H. HALE

Quantitative combustion of hydrocarbons has been continued during the past year and the results confirm the conclusion already reported[1] that the atomic weight of carbon is not far from 12.010.

Only minor changes were made in the combustion apparatus and analytical technique. The ring seal of the second bulb in the water absorption system was eliminated in order that complete equalization of pressure might be more easily secured during weighing. Furthermore, the air in this system was saturated with water during the first weighing, so that no correction was necessary on this score. In some of the analyses (71, 74, 78, 79, 80), a somewhat smaller but similar system was used for absorbing the carbon dioxide, in order to increase the accuracy of weighing.

During the earlier work preliminary experiments had shown that the "blank" corrections were very small. These and later experiments, carried out by passing air and oxygen through the empty combustion tube while it was heated as in the combustions, produced the changes in weight (positive) given in the following tables.

AIR

	Duration of run, hours	H_2O, mg.	CO_2, mg.
	44	0.26	0.38
	64	.52	.62
Total	108	.78	1.00
Gain per hour		.0072	0.0093

OXYGEN

At the close of each run the tubes were swept out with air, and a correction made for the period during which air was used.

	Duration of run, hours	H_2O, mg.	CO_2, mg.
	44	0.76	0.01
	71	.68	1.17
	69	.53	0.90
	80	.73	.81
Total	264	2.70	2.89
Gain per hour		0.0102	0.0109

On the basis of these results in each of the new experiments as well as in those already reported a negative correction based on these blanks has been applied. This correction usually amounted to about 0.1 mg. each for both water and carbon dioxide.

Purification of Hydrocarbons

Pyrene.—Although our earlier attempts to purify pyrene had apparently been unsuccessful, further efforts were made as follows. One specimen after crystallization from pure benzene was first melted in vacuum with freshly fused potassium hydroxide and then distilled from the potassium hydroxide. After another crystallization the sample was melted in nitrogen at low pressure in contact with metallic sodium, and then distilled from the sodium. Crystallization from benzene, distillation at low pressure and another crystallization followed.

Another sample was kept melted, in nitrogen at low pressure, over metallic mercury for twenty hours. This was followed by crystallization from benzene, treatment with sodium as described above, another crystallization, distillation at low pressure and a final crystallization.

The benzene used in these experiments and in the puri-

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(1) Baxter and Hale, THIS JOURNAL, **58**, 510 (1936).

TABLE I

ATOMIC WEIGHT OF CARBON

O = 16.0000 H = 1.0078

Analysis	Sample	Hydrocarbon, g.	H_2O, g.	H, g.	C, g.	CO_2, g.	O, g.	Ratio C:O_2	At. wt. of C
Chrysene									
39	I	2.78052	1.31192	0.14678	2.63374	9.65237	7.01863	0.375250	12.008(0)
40	I	2.69266	1.27591	.14275	2.54991	9.34366	6.79375	.375332	12.010(6)
45	I	2.97790	1.41044	.15780	2.82010	10.33440	7.51430	.375298	12.009(5)
47	I	2.99659	1.41906	.15877	2.83782	10.39868	7.56086	.375330	12.010(6)
66	II	3.01102	1.42558	.15950	2.85152	10.44739	7.59587	.375404	12.012(9)
67	II	2.97646	1.40901	.15764	2.81882	10.32819	7.50937	.375374	12.012(0)
68	II	2.97260	1.40723	.15744	2.81516	10.31566	7.50050	.375330	12.010(6)
70	II	1.56689	0.74145	.08295	1.48394	5.43767	3.95373	.375327	12.010(5)
73	III	3.08222	1.45976	.16332	2.91890	10.69608	7.77718	.375316	12.010(1)
74	III	2.07420	0.98195	.10986	1.96434	7.19819	5.23385	.375315	12.010(1)
							Average	.375328	12.010(5)
Triphenylbenzene									
42	I	3.00022	1.58994	0.17788	2.82234	10.34128	7.51894	0.375364	12.011(6)
44	II	2.99781	1.58711	.17757	2.82024	10.33453	7.51429	.375317	12.010(1)
48	II	2.99647	1.58580	.17742	2.81905	10.33018	7.51113	.375316	12.010(1)
60	III	3.00284	1.58874	.17775	2.82509	10.35196	7.52687	.375334	12.010(7)
61	III	6.00641	3.17865	.35563	5.65078	20.70670	15.05592	.375320	12.010(2)
63	IV	2.99682	1.58563	.17740	2.81942	10.33123	7.51181	.375332	12.010(6)
64	IV	3.00217	1.58866	.17774	2.82443	10.35028	7.52585	.375297	12.009(5)
65	IV	2.99844	1.58649	.17750	2.82094	10.33739	7.51645	.375302	12.009(7)
							Average	.375323	12.010(3)
Anthracene									
55	I	2.99495	1.51439	0.16943	2.82552	10.35385	7.52833	0.375318	12.010(2)
56	I	2.04939	1.03659	.11597	1.93342	7.08535	5.15193	.375281	12.009(0)
62	III	2.87189	1.45078	.16231	2.70958	9.92877	7.21919	.375330	12.010(6)
71	III	2.95847	1.49521	.16729	2.79118	10.22821	7.43703	.375308	12.009(9)
72	III	2.88436	1.45742	.16306	2.72130	9.97193	7.25063	.375319	12.010(2)
76	II	6.06324	3.06430	.34284	5.72040	20.96070	15.24030	.375347	12.011(1)
77	II	5.44882	2.75414	.30814	5.14068	18.83572	13.69504	.375368	12.011(8)
80	II	2.81287	1.42365	.15928	2.65359	9.72451	7.07092	.375282	12.009(0)
81	II	5.54044	2.80123	.31340	5.22704	19.15276	13.92572	.375352	12.011(3)
							Average	.375323	12.010(3)
							Average of all results	.375325	12.010(4)
Pyrene									
78		3.00338	1.33857	0.14976	2.85362	10.44871	7.59509	0.375719	12.023(0)
79		2.99923	1.33674	.14956	2.84967	10.43690	7.58723	.375588	12.018(8)

fications described below had been treated with concentrated sulfuric acid, distilled and three times fractionally frozen.

The two samples of pyrene, when quantitatively burned, yielded 12.023 (Analysis 78) and 12.019 (Analysis 79) for the atomic weight of carbon, results essentially like those previously obtained with pyrene. Apparently these efforts at purification were as unsuccessful as the earlier ones. Actually Dr. E. B. Hershberg was able to detect sulfur in both these samples.

Chrysene.—A portion of the chrysene used in Analyses 39, 40, 45 and 47 of the previous work was further purified by distillation in nitrogen at low pressure and by crystallization from pure benzene (Sample II). The melting point was kindly determined by Dr. Hershberg to be 254.1–254.4°, corr.[2] Before this purification the melting point was 254.5–255.0°, although the composition before the treatment described above was identical with that of this sample.

Through the kindness of Professor L. F. Fieser we received a synthetic sample of chrysene[3] built upon naphthalene as a nucleus. We subjected this sample to three crystallizations from benzene with intermediate distillations at low pressure; m. p. 254.1–254.4° (corr.), Sample III.

Triphenylbenzene.—A portion of Sample II (previous paper, m. p. 174.3–174.5°, corr.) was slowly distilled at very low pressure with rejection of about a gram of slightly yellow residue. The product was once crystallized from pure benzene; m. p. 174.3–174.5° (corr.), Sample III.

A new sample was prepared for us by Dr. M. S. Newman under the direction of Professor Fieser. Benzaldehyde

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(2) All other melting points given in this paper were determined by Dr. Hershberg.

(3) Fieser, Fieser and Hershberg, THIS JOURNAL, **57**, 1851 (1935); **58**, 1463 (1936).

from amygdalin was converted to secondary phenylethyl alcohol with methylmagnesium chloride. Oxidation with dichromate and sulfuric acid yielded acetophenone, and condensation of acetophenone in a sealed tube with hydrochloric acid at 200° yielded triphenylbenzene. The latter was crystallized from acetic acid, distilled at low pressure and crystallized four times from dioxane. We purified the sample further by two crystallizations from benzene, low pressure distillation and a final crystallization from benzene; m. p. 174.2–174.5° (corr.), Sample IV. The sample previously used melted at 174.3–174.5° (corr.).

Anthracene.—A new sample of anthracene was purified as described in our earlier paper, Sample II.

Still a third sample was prepared from phthalic acid and benzene. Phthalic acid, after crystallization from water, was dehydrated to the anhydride. From phthalic anhydride and benzene with aluminum chloride *o*-benzoylbenzoic acid was prepared, and crystallized from benzene. Treatment of the product with concentrated sulfuric acid yielded anthraquinone which was recrystallized from glacial acetic acid. Reduction of anthraquinone to anthrone was effected with tin and hydrochloric acid. After recrystallization from a mixture of benzene and petroleum ether the anthrone was reduced to anthracene with zinc dust, sodium hydroxide and ammonia, and the anthracene was three times recrystallized from benzene. To purify the anthracene further it was melted in contact with potassium hydroxide in nitrogen at low pressure, distilled from the mixture, and crystallized from benzene. These processes were then repeated. Finally the product was melted in nitrogen, distilled at low pressure and recrystallized from pure benzene; m. p. of distilled material, 216.2–216.4° (corr.). The sample previously prepared melted at 216.4–216.7° (corr.), Sample III.

In Table I the weights of hydrocarbon have been corrected to vacuum. The weights of water have been corrected to vacuum, for dissolved air (see preceding paper), and for the blank (see page 506). The weights of carbon dioxide have been corrected to vacuum, and for the blank (see page 506).

A restandardization of the weights brought to light an error in the correction of one of the weights used in the earlier experiments. Because of this, and because "blank" corrections are now available the recalculated results of the earlier experiments are included with the new ones. No experiments are omitted from the table except those abandoned because of some accident.

In most of the analyses about 3 g. of hydrocarbon was burned. This quantity seemed to ensure sufficient accuracy and since seven to nine hours were required for combustion alone of this amount the experiment was as prolonged as it could be without too much tax on the analyst. In four experiments about 6 g. was burned, Nos. 61, 76, 77 and 81. The average result of these four experiments is 12.0111, that is, slightly less carbon dioxide was recovered than in the others. But of these four, Analysis 61 yielded more than the average and the atomic weight 12.0102. In Analyses 56, 70 and 74 only 1.5–2.0 g. was burned. The average of these three is 12.0099, but the average of Analyses 70 and 74 is 12.0103.

In four experiments, Analyses 55, 60, 68 and 77 the rate of burning was less than normal, about twelve hours for 3 g., and the average result 12.0108, while in Analysis 61 6 g. was burned in ten hours, yet Analysis 61 yielded slightly more carbon dioxide than the normal.

It seems unlikely that variations in quantity of hydrocarbon burned or minor variations in speed of combustion had any important effect on the result.

The average atomic weight of carbon (excluding results with pyrene), 12.010, is 0.001 unit higher than that reported in our earlier paper, partly because of the new corrections, partly because the effect of experiments 39 and 56 is distributed over a larger number.

As we have already pointed out, because of the low percentage of hydrogen in our hydrocarbons the method is comparatively insensitive to the present uncertainty in the atomic weight of hydrogen. Aston's[4] recent value, corrected to the chemical scale and for H^2, is 1.0081. With this value for hydrogen, that of carbon is lowered only 0.00026. It seems unlikely that natural variations in isotopic proportions (H, O, C) will be observed large enough to affect present chemical accuracy.

Although in this method it is unnecessary that the hydrocarbons should be pure, but only necessary that they should be free from impurities other than hydrocarbons, the composition of each hydrocarbon seems to correspond very closely with the formula in every case except that of pyrene. In the following table calculations of the percentages of hydrogen and carbon are made from the weights of water and carbon dioxide, with the use of the values 1.0078 and 12.010, for hydrogen and carbon, respectively. For the twenty-seven analyses (those with pyrene excluded) the average net deficiency from the theoretical in hydrogen is 0.0001%, that in carbon 0.002%. This apparent deficiency in carbon necessarily disappears entirely if our average atomic weight, 12.0104, is employed.

Aston's[4] most recent value for C^{12}, converted to the chemical scale with the factor 1.00025, is

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[4] Aston, *Nature*, **137**, 357 (1936).

TABLE II

Analysis	% H	% C	Total
Chrysene, $C_{18}H_{12}$			
39	5.279	94.733	100.012
40	5.301	94.695	99.996
45	5.299	94.704	100.003
47	5.298	94.698	99.996
66	5.297	94.686	99.983
67	5.296	94.693	99.989
68	5.296	94.700	99.996
70	5.294	94.703	99.997
73	5.299	94.701	100.000
74	5.296	94.703	99.999
Average	5.296	94.701	99.997
Calculated	5.298	94.702	
Triphenylbenzene, $C_{24}H_{18}$			
42	5.929	94.062	99.991
44	5.923	94.076	99.999
48	5.921	94.078	99.999
60	5.919	94.077	99.996
61	5.921	94.078	99.999
63	5.920	94.077	99.997
64	5.920	94.082	100.002
65	5.920	94.082	100.002
Average	5.922	94.077	99.999
Calculated	5.921	94.079	
Anthracene, $C_{14}H_{10}$			
55	5.657	94.342	99.999
56	5.659	94.347	100.006
62	5.652	94.345	99.997
71	5.655	94.346	100.001
72	5.653	94.346	99.999
76	5.654	94.339	99.993
77	5.655	94.335	99.990
80	5.663	94.343	100.006
81	5.657	94.336	99.993
Average	5.656	94.342	99.998
Calculated	5.655	94.345	
Pyrene, $C_{16}H_{10}$			
78	4.986	94.939	99.925
79	4.987	94.963	99.950
Calculated	4.983	95.017	

12.0005. This is 1/10,000 lower than the value reported by him a year earlier, 12.0018.[5] Bainbridge (private communication) finds 12.0012, corrected to the chemical scale. With the value 12.0012 for C^{12} and our atomic weight the calculated abundance ratio of C^{13} is 1/109. This value is lower than that computed from our earlier results. Jenkins and Ornstein[6] find 1/106; Vaughan, Williams and Tait[7] 1/92 and Aston[8] 1/138.

Summary

It seems unlikely that our final value would be altered materially by continuance of the experiments. Of the four hydrocarbons investigated, one, pyrene, proved incapable of being purified by any method we could devise. The other three yielded identical results for carbon, whether they had been initially separated from coal tar, or synthesized, from a simple coal tar product in two cases (chrysene and anthracene), from a natural product in the third (triphenylbenzene).

The average atomic weight of carbon obtained by combustion of chrysene, triphenylbenzene and anthracene, 12.010, may therefore be taken as a fair outcome of this method of attack.

CAMBRIDGE, MASS. RECEIVED DECEMBER 14, 1936

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[5] Aston, *Nature*, **135**, 541 (1935).

[6] Jenkins and Ornstein, *Proc. Acad. Sci. Amsterdam*, **35**, 1212 (1932).

[7] Vaughan, Williams and Tait, *Phys. Rev.*, **46**, 327 (1934).

[8] Aston, *Proc. Roy. Soc.* (London), **A149**, 400 (1935).

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

Studies in the Physical Chemistry of the Proteins. XIV. The Amphoteric Properties of Hemoglobin*

BY EDWIN J. COHN, ARDA A. GREEN AND MURIEL H. BLANCHARD

The behavior of proteins is determined largely by the number and distribution of their electrically charged groups. An accurate knowledge of the number of dissociable groups is therefore an essential requisite for the study of their distribution by such means as dielectric constant measurements and measurements of change in activity coefficient with change in ionic strength. In extending to proteins relationships developed by the study of amino acids and peptides, we shall first consider those that can be obtained as pure chemical individuals.

From certain points of view the hemoglobin of the horse may be considered the best known of the proteins. It is readily crystallizable by a number of procedures. It contains 0.335% iron[1] and

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* For supplementary tables of data obtained in this work, order Document 1007 from Science Service, 2101 Constitution Ave., Washington, D. C., remitting 25¢ for microfilm form, or 50¢ for photocopies readable without optical aid.

[1] Zinoffsky, *Z. physiol. Chem.*, **10**, 16 (1886).

0.390% sulfur. The minimal molecular weight of hemoglobin estimated from its sulfur content is 8223, and that from its iron content is double this value, or 16,669. Svedberg and Nichols have studied "the influence of *p*H on the diffusion constant, molecular weight and specific sedimentation velocity of carbon monoxide hemoglobin. . . over a *p*H range of 5.4 to 10.2. The diffusion constant and the specific sedimentation velocity are normal. . . over the range of *p*H 6.0 to 7.56, and the molecular weight is normal, 68,000, at least from a *p*H of 6.0 to 9.05."[2] Osmotic pressure measurements upon aqueous hemoglobin solutions yield the same molecular weight,[3] though it has been suggested that this weight is halved in urea solutions[4] and perhaps under other conditions.

The solubility of horse hemoglobin also has been investigated under a wide variety of conditions, and has been demonstrated to be essentially independent of the amount of saturating body.[5,6,7] Hemoglobin is therefore not only monodisperse, but a chemical individual.

The isoelectric point of hemoglobin has been estimated to be near *p*H 6.8.[8] Its acid properties are increased to the same extent by combination with either oxygen or carbon monoxide, but this effect, important over the physiological range, does not extend to extremely acid or alkaline reactions.

The basic properties of globin depend upon the large amounts of arginine, histidine and lysine in the molecule. Isolation methods have yielded nearly the same values for histidine[9,10] as the nitrogen distribution method[11] (Table I).

The latter method, however, yielded slightly higher estimates for arginine and lysine, suggesting the difficulties of quantitative isolation of these most basic amino acids. The nitrogen distribution method often yields too high values, however. Horse hemoglobin may therefore be assumed to contain between 83 and 93 free basic groups derived from histidine, arginine and lysine.

TABLE I

HORSE HEMOGLOBIN

		Amino acid in hemoglobin hydrolysate, %	Equivalent combining weight per g. hemoglobin moles $\times 10^5$	Weight hemoglobin containing one mole amino acid, g. per moles	Moles amino acid per mole hemoglobin, no. of equivalents
Tyrosine		3.15	17.4	5749	12
Histidine	(10)	7.64	49.3	2030	33
	(9)	7.60	49.0	2041	33
	(11)[a]	7.74	49.9	2004	33
Arginine	(10)	3.32	19.1	5244	13
	(9)	3.60	20.7	4836	14
	(11)[a]	4.11	23.6	4236	16
Lysine	(10)	8.10	55.4	1804	37
	(9)	8.25	56.5	1771	38
	(11)[a]	9.55	65.4	1530	44
Trivalent bases	(10)	19.06	123.8		83
	(9)	19.45	126.2		85
	(11)[a]	21.40	138.9		93

[a] Values by Hunter and Borsook recalculated by Vickery and Leavenworth.[10]

Estimates of the dicarboxylic amino acids in hemoglobin are unfortunately incomplete, or unsatisfactory, but tyrosine has been analyzed by Folin and Marenzi[12] and found to be present to 3.15%. This analysis as well as those of Vickery and Leavenworth[10] were carried out on hemoglobin isolated and recrystallized in this Laboratory by the same methods as the preparations employed in the physical chemical studies.

Materials and Methods.—The method employed in the preparation of hemoglobin has been described repeatedly[6,13] and essentially consists in recrystallization at the isoelectric point. Experiments I to III were carried out with preparations made in 1930, and preparations IV to VIII in 1936.[14]

The repeatedly recrystallized and washed carboxyhemoglobin generally had a *p*H near 6.5. At this reaction, however, horse hemoglobin is relatively insoluble. It was dissolved by the addition of just sufficient sodium hydroxide of known concentration. The *p*H of these stock solutions was generally between 7.4 and 7.8. They were saturated with carbon monoxide and analyzed

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(2) Svedberg and Nichols, THIS JOURNAL, **49**, 2934 (1927).

(3) Adair, *Proc. Roy. Soc.* (London), **A120**, 573 (1928).

(4) Burk and Greenberg [*J. Biol. Chem.*, **87**, 197 (1930)] give the molecular weight of hemoglobin in urea as 34,000, but Huang and Wu [*Chinese J. Physiol.*, **4**, 221 (1930)] give the molecular weight of hemoglobin in this solvent as 66,200. Steinhardt [*Nature*, **138**, 800 (1936)] has recently studied hemoglobin in urea solutions with the ultracentrifuge and reported a value close to 34,000.

(5) Cohn and Prentiss, *J. Gen. Physiol.*, **8**, 619 (1927).

(6) Green, *J. Biol. Chem.*, **93**, 495; **93**, 517 (1931); **95**, 47 (1932).

(7) Sörensen and Sörensen, *Compt. rend. trav. Lab. Carlsberg*, **19**, No. 11 (1933).

(8) Michaelis, "Nernst Festschrift," Verlag Wilh. Knapp, Halle an der Saale, Germany, 1912; *Biochem. Z.*, **47**, 250 (1912). Ferry, *J. Biol. Chem.*, **57**, 819 (1923).

(9) Abderhalden, Fleischmann and Irion, *Fermentforschung*, **10**, 446 (1929).

(10) Vickery and Leavenworth, *J. Biol. Chem.*, **79**, 377 (1928).

(11) Hunter and Borsook, *ibid.*, **57**, 507 (1923). The values of Hunter and Borsook by the nitrogen distribution method have been recalculated by Vickery and Leavenworth.

(12) Folin and Marenzi, *ibid.*, **83**, 89 (1929).

(13) Ferry and Green, *ibid.*, **81**, 175 (1929).

(14) These preparations were made by Ferry and Newman for studies on the solubility of hemoglobin in ethanol–water mixtures. Ferry, Cohn and Newman, *J. Biol. Chem.*, **114**, Proc. xxxiv (1936).

for the small remaining amounts of chloride and for total nitrogen. The nitrogen content of horse hemoglobin is taken as 16.86%.[10] The amounts of sodium chloride recorded in Tables II and III include, in the case of acid titrations, the neutralized alkali used to dissolve the hemoglobin.

TABLE II

ELECTROMOTIVE FORCE MEASUREMENTS ON SYSTEMS CONTAINING CARBOXYHEMOGLOBIN AND HYDROCHLORIC ACID

HCl concn. moles/liter	Log $1/a_{H^+}$, pH^+	Log $1/C_{H^+}$, $pH^+ - p\gamma_{H^+}$	HCl uncombined, moles/liter	HCl combined, moles/liter	HCl combined, moles $\times 10^5$ per g. Hb
Experiment III: 48.8 g. Hb and 0.01 mole NaCl per liter					
0.0625	2.994	2.929	0.0012	0.0609	124.8
	2.965	2.900	.0013	.0608	124.6
.0701	2.610	2.542	.0028	.0672	137.7
	2.613	2.545	.0028	.0672	137.7
.0901	1.827	1.751	.0177	.0724	148.4
	1.823	1.747	.0179	.0722	144.0
Experiment III: 10.84 g. Hb and 0.0022 mole NaCl per liter					
0.0173	2.677	2.631	0.0023	0.0150	138.4
	2.656	2.610	.0025	.0149	137.5
.0213	2.300	2.252	.0056	.0157	144.8
	2.303	2.255	.0056	.0158	145.8
.0253	2.103	2.054	.0088	.0165	152.2
	2.080	2.031	.0093	.0160	147.6
.0273	1.996	1.946	.0113	.0160	137.6
	2.000	1.950	.0112	.0161	148.5
.0293	1.922	1.871	.0135	.0159	146.7
	1.934	1.883	.0131	.0163	150.4
Experiment IV: 20.95 g. Hb and 0.0042 mole NaCl per liter					
0.0368	2.239	2.186	0.0065	0.0303	144.6
	2.234	2.181	.0066	.0302	144.2
.0448	1.910	1.854	.0140	.0308	147.0
	1.915	1.859	.0138	.0310	148.0
.0568	1.644	1.584	.0261	.0307	146.5
	1.645	1.585	.0260	.0308	147.0
.0684	1.491	1.426	.0375	.0309	147.5
	1.496	1.431	.0371	.0313	149.4

The varying amounts of standard acid or alkali were added to aliquot parts of the stock carboxyhemoglobin solutions and brought to constant volume shortly before they were transferred to hydrogen electrodes. Clark hydrogen electrode vessels, 0.1 *N* calomel electrodes and a saturated potassium chloride salt bridge were employed, no correction being made for the liquid junction potential. The electrodes were always standardized with 0.1 *N* hydrochloric acid, the *p*H of which was considered to be 1.075.[15] Four different electrodes were used, measurements generally being made in duplicate.

TABLE III

ELECTROMOTIVE FORCE MEASUREMENTS ON SYSTEMS CONTAINING CARBOXYHEMOGLOBIN AND SODIUM HYDROXIDE

NaOH Concn., moles/liter	Log $1/a_{H^+}$, $pH^+_{25°}$	Log $1/C_{OH^-}$, $p_{OH^-} - p\gamma_{OH^-}$	NaOH uncombined, moles/liter	NaOH combined, moles/liter	NaOH combined, moles $\times 10^5$ per g. Hb
Experiment IV: 20.95 g. Hb and 0.0027 mole NaCl per liter					
0.0430	12.140	1.688	0.0205	0.0225	107.4
	12.142	1.686	.0206	.0224	106.9
.0629	12.398	1.420	.0380	.0249	118.9
	12.408	1.410	.0389	.0240	114.6
	12.390	1.428	.0373	.0256	122.2
.0828	12.586	1.224	.0597	.0231	110.3
	12.583	1.227	.0593	.0235	112.2
	12.571	1.239	.0577	.0251	119.8
	12.593	1.217	.0607	.0221	105.5
	12.593	1.217	.0607	.0221	105.5
.0987	12.693	1.111	.0774	.0213	101.7
	12.684	1.120	.0759	.0228	108.8
Experiment VI: 18.54 g. Hb and no NaCl added					
0.0676	12.494	1.323	0.0475	0.0201	103.3
.0836	12.603	1.207	.0621	.0215	116.0
	12.619	1.191	.0644	.0192	103.5
Experiment VI: 27.80 g. Hb and no NaCl added					
0.06522	12.334	1.483	0.0329	0.0323	116.3
.08516	12.535	1.274	.0532	.0320	114.9
.10510	12.651	1.151	.0706	.0345	124.0

Calculation of Results.—Acid and base combined by protein is calculated as the difference between the total and the free acid, C_{H^+}, or base C_{OH^-}, present. This calculation involves the activity coefficients of the hydrogen and hydroxyl ions, which were estimated by Lewis and Randall[16] from mean activity coefficients on the assumption that γ_{H^+} is equal to γ_{OH^-} in solutions more dilute than 0.01 *N*. They estimate $-\log \gamma_{H^+}$ in 0.1 *N* hydrochloric acid as 0.076. Scatchard's[15] subsequent revision yields slightly higher values for $-\log \gamma_{H^+}$ at low concentrations, but his result, 0.075, is in good agreement at 0.1 *N*. The standardization of our electrodes with 0.1 *N* hydrochloric acid has always given a value close to this for the hydrogen potential.[17]

"Although Lewis and Randall's . . . value 1.005 × 10^{-14} . . . is now the most probable value for the dissociation constant of water, its use in the calculation of our data leads to different values for p_{OH^-} in alkaline solution than those calculated from Lewis and Randall's coefficients for the activity of the hydroxyl ion. In all probability this de-

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(15) Scatchard, THIS JOURNAL, **47**, 696 (1925).

(16) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," 1st ed., McGraw-Hill Book Company, Inc., New York, 1923.

(17) Cohn and Berggren, *J. Gen. Physiol.*, **7**, 45 (1924).

pends not upon the value of K_w, but upon diffusion potentials, for which we have not corrected. If, however, we employ the Sørensen–Michaelis values for K_w at different temperatures, our p_{OH}-values conform approximately to those calculated from the activity of the hydroxyl ion"[17] (p. 53). Without making any assumption whatever as to the correct value for K_w we have adopted tentatively the latter.[18] The temperature variation of pH is also ascribed to K_w, and not to p_{OH}-(pK_w − pH$^+$).

The activity coefficients of the hydrogen and hydroxyl ions depend not only on their concentrations, but on those of all other ions in solution and decrease as the valency of the latter increases. Thus the higher valencies of protein anions and cations might be expected to have a large effect on the activity coefficients of the hydrogen and hydroxyl ion. In an attempt to evaluate the kind of correction that should be employed in studies of amino acids and proteins, we studied some years since the activity coefficients of the hydroxyl ion in sodium hydroxide solutions containing other sodium compounds, including "four bivalent acids, sulfuric, oxalic, glutamic, and aspartic, the two latter amino acids. . . . The results with these acids. . . suggest that anions of higher valence have greater effects upon the activity of the hydroxyl ion. This effect might be expected to increase with the ionic strength, but the effect on the amino acids studied at this concentration was not so great as that of other divalent salts. . . . Because of their high valence, protein anions may, of course, further depress the activity of the hydroxyl ion. Uncertainty regarding the valence type to be ascribed to proteins makes it difficult, however, to apply a correction for this factor, and their very low concentration may make it unnecessary. Accordingly we have tentatively used the values of γ deduced from measurements of sodium hydroxide solutions in the calculation of our data"[17] (p. 57).

There is no doubt that activity coefficients, calculated on the basis of inorganic ions, are too low. There is also no doubt that those calculated on the basis of the valence of protein salts are far too high. Recent studies on the effect of the sodium salts of proteins, including hemoglobin, on the solubility of thallous chloride have been reported by Stone and Failey. Their results confirm the above conclusion, for the activity coefficients of the thallous chloride are far smaller than would be expected on the basis of ionic strengths calculated in terms of the molecular weights and the number of free groups of proteins. They calculated base combining capacity by assuming the mean activity coefficient of the thallous chloride, as determined by these solubility measurements, to yield the activity coefficient of the hydroxyl ion.[19]

In all of these methods, the activity coefficient of the hydroxyl ion varies with the sodium hydroxide concentration, and with the protein concentration. In order to minimize the influence of these factors we have carried out measurements in systems normal with respect to sodium chloride

TABLE IV

ELECTROMOTIVE FORCE MEASUREMENTS ON SYSTEMS CONTAINING CARBOXYHEMOGLOBIN, SODIUM HYDROXIDE AND MOLAL SODIUM CHLORIDE

NaOH concn., moles/liter	Log $1/a_{H^+}$, $pH^+_{25°}$	Log $1/C_{OH^-}$, $p_{OH^-} - p\gamma_{OH^-}$	NaOH uncombined, moles/liter	NaOH combined, moles/liter	NaOH combined, moles $\times 10^5$ per g. Hb
Experiment V: 16.37 g. Hb per liter					
0.0400	12.015	1.650	0.0224	0.0176	107.5
.0560	12.229	1.436	.0366	.0194	118.5
.0800	12.459	1.206	.0622	.0178	108.7
.1200	12.676	0.989	.1026	.0174	106.3
Experiment VI: 27.80 g. Hb per liter					
0.08516	12.395	1.260	0.0550	0.03016	108.5
.10510	12.550	1.116	.0766	.02850	108.5
.12504	12.646	1.019	.0957	.02934	105.5
Experiment VII: 19.30 g. Hb per liter					
0.05982	12.258	1.407	0.0392	0.02062	106.8
	12.250	1.415	.0385	.02132	110.5
	12.263	1.402	.0396	.02022	104.8
	12.253	1.402	.0387	.02112	109.4
.09970	12.560	1.105	.0785	.02120	109.8
	12.564	1.101	.0793	.02040	105.7
.11964	12.664	1.001	.0998	.01984	102.8
	12.666	0.999	.1002	.01944	100.7
.15872	12.803	.862	.1374	.02132	110.5
	12.809	.856	.1393	.01942	100.6
Experiment VIII: 48.08 g. Hb per liter					
0.074410	12.028	1.637	0.0231	0.05131	106.7
	12.026	1.639	.0230	.05141	106.9
.08434	12.196	1.469	.0340	.05034	104.9
	12.190	1.475	.0335	.05084	105.7
.12411	12.535	1.130	.0741	.05001	104.0
	12.526	1.139	.0726	.05151	107.1
.24345	12.958	0.707	.1963	.04715	98.1
	12.958	.707	.1963	.04715	98.1
.28323	13.034	.631	.2339	.04933	102.6

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(18) For interpolated values of $-\log K_w$ see W. Mansfield Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1928.

(19) Stone and Failey, *J. Phys. Chem.*, **37**, 935 (1933). Hydrolysis of the hemoglobin may, of course, have occurred during the long times of equilibration for the solubility measurements.

from acidities at which the hemoglobin chloride is precipitated by the neutral salt, to reactions at which the hemoglobin is completely bound by base.

Under these conditions the effect on the activity coefficient, due to the influence of the neutral salt on the hydroxyl ion, is sufficiently large to mask the changes due to variation with sodium hydroxide and presumably with protein concentration. "It has been shown that the Nernst formula for electromotive force, the solubility product and mass action law in the case of a complicated ionic equilibrium are applicable in their classical form to such concentrated salt solutions, the reason for this simplicity being the practical constancy of the activity coefficients in the practically constant medium. Utilization of these results would mean in many cases a great simplification in problems pertaining to electrolytic solutions"[20] (p. 431). Measurements upon 0.01 and 0.1 N sodium hydroxide in N sodium chloride, calculated by means of the Michaelis values of K_w, yield values of $-\log\gamma_{OH}$ which vary less than 0.01 and may be taken as 0.23 at 25° for all the systems containing salt that are reported.

Maximal Acid and Base Combining Capacity of Hemoglobin.—Several studies of the combination of hemoglobin with acid and base have been reported. One of these is the titration with the quinhydrone electrode by Lewis[21] of the carboxyhemoglobin of the ox with sulfuric acid in the presence of ammonium sulfate. His results yield an acid combining capacity of 145×10^{-5} equivalent per gram of hemoglobin. Pauli and Schwarzacher[22] report that hemoglobin combines 159×10^{-5} mole hydrochloric acid per gram and 124.5×10^{-5} mole lithium hydroxide per gram. The results of Stone and Failey[19] yield a base combining capacity of slightly over 100×10^{-5} mole per gram calculated on the basis of the activity coefficient of thallous chloride and the value 14 for pK_w. Recalculation by the methods we have employed yields essentially the same result.

In several experiments we have titrated carboxyhemoglobin to saturation with hydrochloric acid (Table II). No appreciable increase in acid combining capacity was detected at reactions acid to pH 2.2. From pH 2.2 to 1.5 the free hydrochloric acid increased more than sixfold, with a change in combined hydrochloric acid only from 144.6 to 150.4×10^{-5} mole per gram. These results, as calculated, yield a maximal acid combining capacity of 148×10^{-5} mole per gram. The influence of protein in increasing the activity coefficients employed would result in a lower estimate of the combining capacity. The measurements in Table II are subject to correction at such a time as data are available for the activity coefficients of the hydrogen ion in the presence of hemoglobin hydrochloride.

The base combining capacity of hemoglobin has been calculated in Table III. The base bound by hemoglobin increased until the reaction was more alkaline than pH 12.2. At this reaction the concentration of free and combined base was approximately equal. At pH 12.68 the free base was three times that bound, and no appreciable increase in combining capacity was observed, provided the measurements were made soon after the hemoglobin was exposed to such extremely alkaline reactions. In either strongly acid or basic solutions, the hemoglobin changed from its characteristic red color to a deep brown. At either longer times or more alkaline reactions, greater apparent base combining capacities were noted and ascribed to hydrolysis. This was the case with many of the earlier experiments, which yielded satisfactorily constant acid combining capacities, but apparent base combining capacities which varied from experiment to experiment and were always greater than those reported.

The use either of higher activity coefficients, such as those employed by Stone and Failey, or of a larger value for pK_w, would result in lower estimates of base combining capacity than the value which results from the mode of calculation we have always employed (Table III). It was largely to test this point that measurements were undertaken in the presence of normal sodium chloride (Table IV).

Hemoglobin preparations V to VIII were studied in molal sodium chloride. Although the hemoglobin in these experiments varied from 16.37 to 48.08 g. per liter, the results with all but preparation V (which yielded a normal titration curve, but a maximal combining capacity of 148×10^{-5} mole sodium hydroxide per gram, and is not reported in detail since unconfirmed by any subsequent experiment) yield the same or slightly lower maximal combining capacity in the pres-

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(20) Brönsted, *Trans. Faraday Soc.*, **23**, 416 (1927). See also Harned, "The Electrochemistry of Solutions," in Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, Vol. I, 1931, p. 805.

(21) Lewis, *Biochem. J.*, **21**, 46 (1927).

(22) Pauli and Schwarzacher in Pauli and Valkó, "Kolloidchemie der Eiweisskörper," Theodor Steinkopff, Leipzig, 1933.

ence of N sodium chloride as had the earlier experiments on systems to which no salt was added. The base combining capacity in the systems containing normal sodium chloride appears to pass through a minimum near pH 12.3. The apparent decrease in combined base at more alkaline reactions suggests that the activity coefficients employed may have been too large. The curve in Fig. 1 is constructed as though hemoglobin dissociated 261 × 10^{-4} mole of hydrogen ions between pH 1.5 and 13.

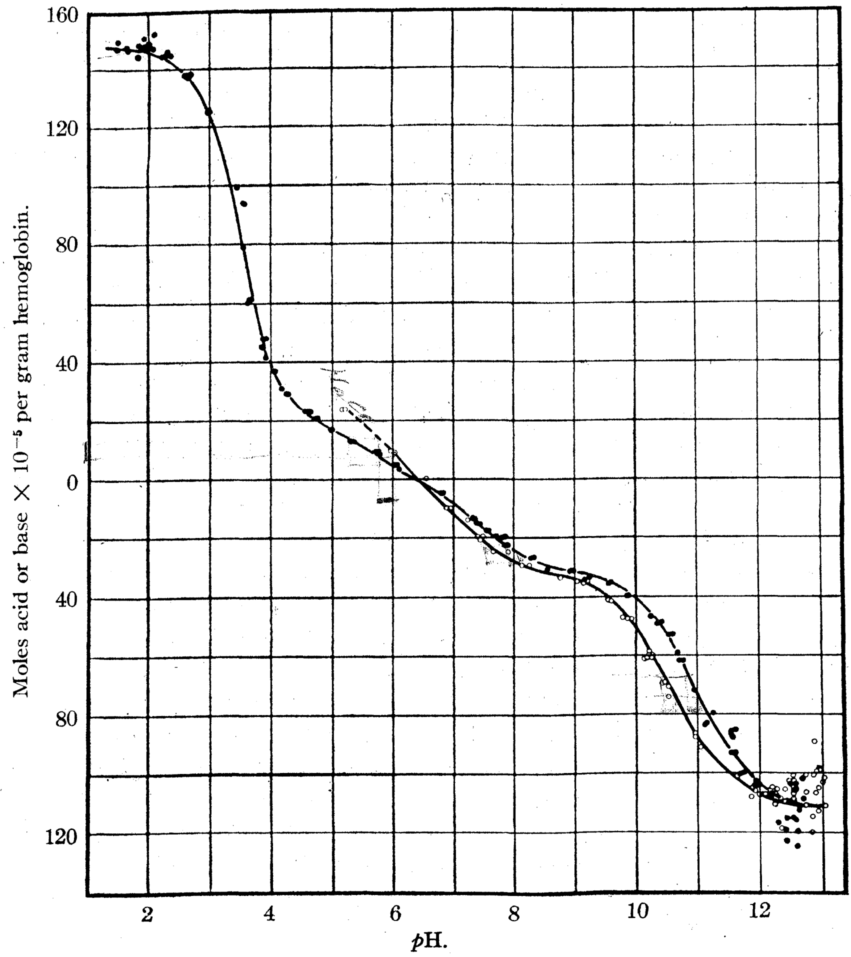

Fig. 1.—The titration curve of carboxyhemoglobin of the horse in the absence of added salt ● and in the presence of 1 M NaCl ⊙.

TABLE V

Protein	Acid combining capacity, moles × 10^5	Base combining capacity, moles × 10^5	Total combining capacity, moles × 10^5
Ox-oxyhemoglobin (21)	145		
Horse—carboxyhemoglobin (19)	159	105 124.5	283.5
(22)	148	113	261

These results are compared with those previously reported in Table V. The final column gives the total acid and base combining capacity of hemoglobin.

Titration Curve of Hemoglobin and its Apparent Dissociation Constants.—Although the acid combining capacity of a protein depends on the histidine, arginine and lysine in the molecule, these basic amino acids dissociate at alkaline reactions. The titration curve of hemoglobin,[23] given in Fig. 1, is readily divisible into at least three well-defined sigmoid curves, one extending from saturation with acid roughly to pH 5, the second from pH 5 to 9 and the third from pH 9 to saturation with base. Although analyzable into a larger number of component parts, we have preferred describing this curve—and that in the presence of N sodium chloride—in terms of the smallest possible number of dissociation constants. The curve in the absence of salt in Fig. 1 is constructed on the basis of the following groups.

Taking the molecular weight of hemoglobin as 67,000, each free reactive group combines with 1.5 × 10^{-5} mole of acid or base per gram. On this basis one may assume 12 tyrosine, from 13 to 16 arginine and from 37 to 44 lysine

TABLE VI

pK_1'	pK_2'	pK_3'	pK_4'	pK_5'	pK_6'	pK_7'
3.7	4.0	4.8	5.7	7.5	10.8	11.6
Number of groups of each constant dissociating						
83		4	13	20	40	14
Carboxyl groups			Histidine		Lysine and Arginine or Tyrosine	

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[23] The large number of measurements at neutral reactions, on which the titration curve is constructed, are not reported in detail for lack of space, but have been filed as a Science Service Document.

molecules per hemoglobin molecule on the basis of the analyses in Table I.

The solid curve in Fig. 1 is constructed on the assumption that 60×10^{-5} mole dissociate with a *p*K of 10.8 and 21×10^{-4} mole with a *p*K of 11.6. In the free condition the *p*K of the ε-amino group of lysine is 10.53 and of the guanidine nucleus 12.48.[24]

The hydroxyl group of tyrosine dissociates at *pK* 10.28[25] and analytical data suggest 12 molecules of tyrosine in the hemoglobin molecule. The titration curve does not reveal a sufficient number of dissociable groups in the range alkaline to *p*H 9 to account for arginine, lysine and tyrosine,[26] but enough to account for lysine and either tyrosine or arginine. Groups dissociating beyond *p*H 13 would not, it is true, be described by our measurements. The experimental errors at more alkaline reactions are, however, formidable.

The unusual feature of the titration curve of hemoglobin is the extremely well-defined sigmoid curve in the neutral range. This part of the curve has previously been investigated by Hastings,[27] and Sörensen,[7] and is now being reinvestigated by German and Wyman[28] by means of the glass electrode, over the region in which it is shifted to more acid reaction as a result of combination with oxygen or carbon monoxide.

Hemoglobin combines with almost exactly 50×10^{-5} mole per gram between *p*H 5 and 9. That is to say, over this range 33 groups dissociate on the hemoglobin molecule, or exactly the number of histidine molecules revealed by analysis. The difference in dissociation of reduced and carboxyhemoglobin does not involve as many as 33 groups. The free group of histidine has a *pK* of 6.04.[24] In histidyl-histidine the comparable groups have dissociation constants of *p*K 5.6 and 6.8.[29] The titration curve in Fig. 1 is constructed by assuming 12 groups dissociating with *pK* 5.6 and 21 groups with *pK* 7.4. The latter groups, or a portion of them, may be considered as combining less acid in the oxygenated than in the reduced state, and as arranged with some sort of symmetry with respect to the four hematin groups of the hemoglobin molecule.[30]

The basic amino acids revealed by analysis suffice to account for the groups dissociating from *p*H 5 to saturation with base. Over this range 87 groups per molecule dissociate. From this reaction to saturation with acid (Table II) roughly the same number of groups would appear to dissociate.

Since phenolic hydroxyl groups do not generally dissociate in a range more acid than *p*H 5, all of the rest of the groups have been assumed to be carboxyl groups. The curve, acid to *p*H 5, is a sigmoid curve with a point of inflection near *p*H 3.6. Amino acid and protein titration curves are generally analyzed by assuming the independence and additivity of the groups dissociating.[31] The most acid segment of the hemoglobin curve appears to be too steep to be accounted for in this manner, suggesting that the acid groups are not independent of each other. Larger activity coefficients, and therefore a smaller acid combining capacity and estimate of dissociable carboxyl groups, might yield a simpler form of sigmoid curve. The curve tentatively has been described in terms of an equation of the type previously suggested, having the form[32]

$$\frac{A^{-n}}{(\mathrm{H}_nA)} = \frac{K_1}{(\mathrm{H}^+)\gamma_1} + \frac{2K_1K_2}{(\mathrm{H}^+)^2\gamma_2} + \frac{3K_1K_2K_3}{(\mathrm{H}^+)^3\gamma_3} + \cdots \\ \frac{nK_1K_2K_3 \ldots K_n}{(\mathrm{H}^+)^n\gamma_n}$$

The first two right-hand terms suffice, *pK*$_1$ being taken as 3.7, and *pK*$_2$ as 4.0. The total curve fits somewhat better if a small number of groups—possibly representing four of the groups of hematin—is assumed to dissociate in the neighborhood of *p*H 4.9.

Influence of Sodium Chloride upon the Titration Curve.—Apparent dissociation constants are not independent of hemoglobin or of salt concentration. In the systems reported salt concentration was maintained below 0.01 *N*, and hemoglobin concentration varied from 10.8 to 88 g. per liter. Over this range, no large effect of protein concentration was observed, but the largest effect of hemoglobin upon its dissociation occurs at very low concentrations, at which it is not practicable to work in strongly acid or alkaline solutions. The influence of sodium chloride concentration on *p*H in systems differing from each other only in re-

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(24) Schmidt, Kirk and Appleman, *J. Biol. Chem.*, **88**, 285 (1930).

(25) Simms, *J. Gen. Physiol.*, **11**, 629 (1928).

(26) Lewis[21] titrated the carboxyhemoglobin of the ox in the presence of formaldehyde with the glass electrode. His results suggest a base combining capacity of 63 moles per mole hemoglobin. This is half again as great as that to be expected from the lysine present.

(27) Hastings, Sendroy, Murray and Heidelberger, *J. Biol. Chem.*, **61**, 317 (1924).

(28) German and Wyman, *ibid.*, **117**, 533 (1937).

(29) Greenstein, *ibid.*, **93**, 479 (1931).

(30) Pauling, *Proc. Nat. Acad. Sci.*, **21**, 186 (1935).

(31) Von Muralt, THIS JOURNAL, **52**, 3518 (1930); Simms, *ibid.*, **48**, 1239 (1926); Weber, *Biochem. Z.*, **189**, 381 (1927).

(32) Cohn, *Physiol. Rev.*, **5**, 349 (1925).

spect to concentration of electrolyte is given in Fig. 2. The smallest effect of salt on the *p*H of protein solutions is near the isoelectric point, as pointed out by Sörensen, and is opposite in direction on either side of the isoelectric point.[5,33,34]

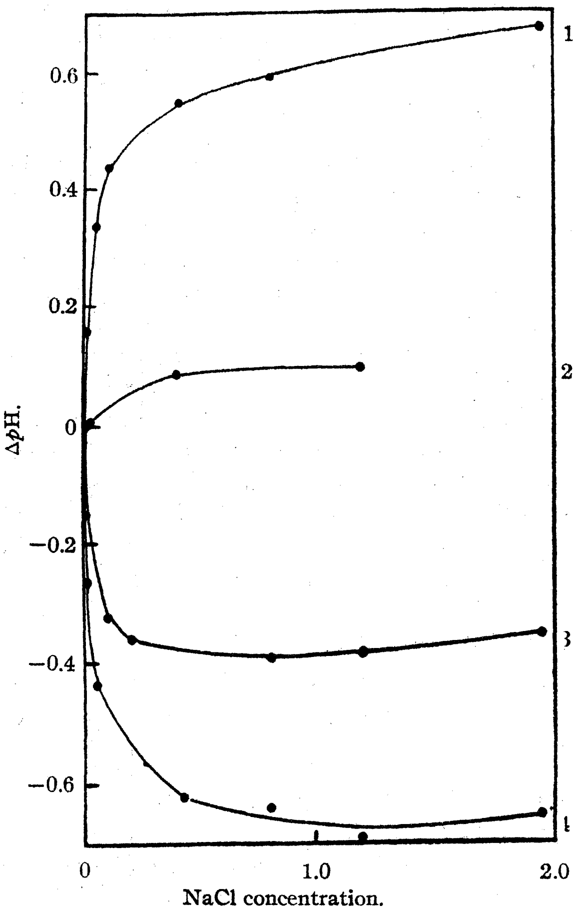

Fig. 2. *Influence of NaCl on the pH of Hemoglobin Solutions.*—Change in *p*H with increasing salt concentration, Δ*p*H, measured at 37° with glass electrode standardized with 0.1 *M* phosphate buffers. The *p*H of the hemoglobin solutions to which no salt was added were: (1) 4.90; (2) 6.60; (3) 7.73; (4) 8.7.

The titration curve in the presence of 1 *M* sodium chloride (Fig. 1) is constructed using the values of 5.2, 6.1, 7.1, 10.4 and 11.2 for pK_3', pK_4', pK_5', pK_6' and pK_7', respectively. pK_3' and pK_4' are thus 0.4 greater and pK_5', pK_6' and pK_7' are 0.4 less than the values in Table IV. Although apparent dissociation constants vary with temperature, salt and protein concentration, total base combining capacity we calculate to be independent of the presence or absence of salt.

Relation between Acid and Basic Dissociation and the Isoelectric Point.—The method of calculation that has been employed may be expected to yield a maximal estimate of dissociable groups.[35] The number of these derived from the histidine may be considered well known. It follows that basic groups dissociate on both sides of the isoelectric point, which bears no simple relation to the reaction, near *p*H 5, on the one side of which acid and on the other side basic groups are presumably dissociating. That certain of the free groups of basic amino acids dissociate in the protein at acid reactions previously has been noted.[36]

The dipolar ion structure of amino acids and proteins demanded reinterpretation of the reactions at which the various groups dissociate. Such analyses of titration curves have been reported,[36–38] but it has often been assumed that the apparent dissociation constants of protein groups bear simple relation to the true dissociation constants of the groups of the free amino acids, a conclusion which by no means follows. The apparent dissociation constants of proteins, as of amino acids and peptides, vary with the number and distribution of the dissociable groups on the molecule.[31–32] The basic strength of an amino group is diminished by carboxyl groups and this is true whether the latter are dissociated or in the non-dissociated condition. Conversely, carboxyl dissociation is increased by juxtaposition of amino and carboxyl groups, and most other substituents. The result is that the closer amino and carboxyl groups are to each other, the more acid the molecule. On the basis of analytical data, casein has half again as many free carboxyl as basic groups, and gelatin twice as many basic as carboxyl groups. In egg albumin the numbers of free acid and basic groups are nearly equal. None the less, all of these proteins have very nearly the same isoelectric point.

Relation between Basic Groups and Acid Combining Capacity, and between Acid Groups and Base Combining Capacity.—In earlier investigations the relation between the number of basic groups and acid combining capacity and between the number of acid groups and base combining

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(33) Sörensen, Höyrup, Hempel and Palitzsch, *Compt. rend. trav. Lab. Carlsberg*, **12**, 68 (1917).

(34) Sörensen, Linderstrøm-Lang and Lund, *J. Gen. Physiol.*, **8**, 543 (1927).

(35) If larger activity coefficients were assumed, not only the base combining but the acid combining capacity would be smaller. The possibility of measuring these activity coefficients by the simultaneous use of cells without liquid junction remains to be accomplished. See Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926), and Joseph, *J. Biol. Chem.*, **111**, 479, 489 (1935).

(36) Simms, *J. Gen. Physiol.*, **14**, 87 (1930).

(37) Kerwick and Cannan, *Biochem. J.*, **30**, 227 (1936).

(38) Russell and Cameron, THIS JOURNAL, **58**, 774 (1936).

capacity has been stressed.[17,32] Reinterpretation of the regions in which the free groups of proteins dissociate in no way alters this relation. Indeed new analyses of the amino acids[39] in proteins have on the whole confirmed the estimates of the number of free groups derived from physical chemical measurements.[40]

Our measurements yield an acid combining capacity of 148 × 10^{-5} and a base combining capacity of 113 × 10^{-5} mole per gram of carboxyhemoglobin. The total combining capacity of 261 × 10^{-5} mole per gram thus represents 174 ± 2 dissociable groups on the hemoglobin molecule, of which 75 would be acid and 99 basic groups. On this basis not more than 75 dipole pairs can be considered dissociated at the isoelectric point.

There remains a discrepancy between these results and those derived from analytical data, for whereas no more than 85 basic amino acids have been isolated from hydrolysates, or 93 estimated by the nitrogen distribution method (Table I), the acid combining capacity suggests the presence of 99 trivalent basic amino acid groups in the hemoglobin molecule.[41] Some of these might conceivably titrate only after partial splitting of the molecule in acid solution, where heme is liberated from globin and the latter yields molecules of smaller molecular size.

Summary

1. Electromotive measurements have been made with the hydrogen electrode on systems containing carboxyhemoglobin and sodium hydroxide and hydrochloric acid.

2. The methods of calculating the combining capacity of a protein from such measurements is discussed, and the acid combining capacity estimated to be 148 × 10^{-5}; the base combining capacity 113 × 10^{-5} mole per gram.

3. On the basis of a molecular weight of 66,700 hemoglobin thus has 174 dissociable groups. Of these not more than 75 dipole pairs can exist at the isoelectric point.

4. Since various analyses reveal between 83 and 93 trivalent basic amino acids per mole of hemoglobin, approximately half the dissociable groups in hemoglobin are derived from the imino group of histidine, the guanidine nucleus of arginine and the ε-amino group of lysine.

5. The free groups of arginine and lysine dissociate at very alkaline reaction, but those of histidine near neutrality. There are 33 histidine molecules in hemoglobin. The free groups of approximately 13 of these appear to dissociate at reactions acid to the isoelectric point. Not more than the remaining 20 dissociate at physiological reactions, in the regions affected in dissociation by oxygenation and reduction of the hemoglobin.

6. The titration curve reported is described in terms of the following pK' values: 3.7, 4.0, 4.8, 5.7, 7.5, 10.8, 11.6. Of these the first three are considered to represent acid groups, the next two histidine groups, and the most alkaline lysine and tyrosine or arginine groups.

7. Although the titration curve is very sensitive to ionic strength, the maximal base combining capacity is demonstrated to be the same in solutions to which no salt was added and in N sodium chloride.

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(39) Among them investigations of the dicarboxylic amino acids of edestin [Jones and Moeller, *J. Biol. Chem.*, **74**, Proc. liv (1927)] and of egg albumin [Calvery, *J. Biol. Chem.*, **94**, 613 (1932)] and of the basic amino acids of the latter protein [Calvery, *ibid.*, and Vickery and Shore, *Biochem. J.*, **26**, 1101 (1932)].

(40) The acid combining capacity of zein, not detected in aqueous systems in which the protein is insoluble [Cohn, Berggren, Hendry, *J. Gen. Physiol.*, **7**, 81 (1924)] has been investigated in the dry state with gaseous hydrogen chloride [Czarnetzky and Schmidt, *J. Biol. Chem.*, **105**, 301 (1934)], and in ethanol–water mixtures [Cohn, Edsall and Blanchard, *ibid.*, **105**, 319 (1934)], and reveals approximately the number of basic groups previously estimated to be present from the results of analyses. See also Neuberger, *Biochem. J.*, **28**, 1982 (1934).

(41) Note added to proof: This discrepancy suggested that part of the acid combining capacity might be ascribable to the heme. Accordingly a study of the acid combining capacity of globin was undertaken and the first preparation investigated combined 138 × 10^{-5} mole per gram, representing 92 free basic groups, or almost exactly those expected from the analyses of basic amino groups in globin and hemoglobin. Other differences between the titration curves of globin and hemoglobin will be reported subsequently.

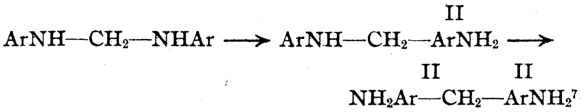
[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Condensations of Aromatic Amines with Formaldehyde in Media Containing Acid. IV. The Conversion of Diarylaminomethanes to Substituted Dihydro- and Tetrahydroquinazolines in Non-Aqueous Media

BY J. K. SIMONS[1]

Interaction of aromatic amines with formaldehyde in media containing acid generally has been assumed to proceed with the primary formation of diarylaminomethane (diimine), $(ArNH)_2CH_2$ or Schiff base, $ArN{=}CH_2$ $\left(\text{or } \left(\begin{matrix}\text{ArN—CH}_2\\ |\quad\;\; |\end{matrix}\right)_n\right)$.[2] The end-products of the condensation, however, appear to be the results of further reactions induced by the instability in an acid medium of the grouping $>N{-}CH_2{-}N<$[2]. Among these secondary reactions is the isomerization of the diimine (or Schiff base) to the aminobenzylaniline or diphenylmethane bases.[3]

The aminobenzylaniline base may be obtained as major product from a mixture of the diimine or Schiff base with the corresponding amine and amine salt under mild conditions and in the absence of water.[4] At higher temperatures essentially the same reaction mixture yields the diphenylmethane base,[4,5] and as this is formed also if the aminobenzylaniline base is used instead of the diimine (or Schiff base)[6] it is obvious and is generally accepted that the entire transformation involves two well defined steps

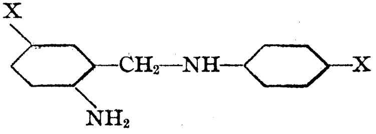


$$\text{ArNH—CH}_2\text{—NHAr} \longrightarrow \text{ArNH—CH}_2\text{—}\overset{\text{II}}{\text{ArNH}_2} \longrightarrow \overset{\text{II}}{\text{NH}_2\text{Ar}}\text{—CH}_2\text{—}\overset{\text{II}}{\text{ArNH}_2}{}^{7}$$

These behaviors appear to be general for aromatic primary amines and secondary amines of the type ArNHR, whether or not the para hydrogen is substituted. It has been shown, however, that in the case of *p*-toluidine the second stage of the reaction occurs less readily than with amines without para substituents.[3] It was therefore thought that the first step, *e. g.*, conversion of di-*p*-toluidinomethane or of methylene-*p*-toluidine to *o*-amino-*m*-xylyl-*p*-toluidine, could be studied separately under a variety of conditions with a view to the positive elucidation of the mechanism of the change. Accordingly di-*p*-toluidinomethane was allowed to react at 80–90° with toluidine and toluidine hydrochloride with the unexpected result that the products of the reaction were 3-*p*-tolyl-6-methyl-3,4-dihydroquinazoline, 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline, *o*-amino-*m*-xylyl-*p*-toluidine, *p*-toluidine and methyl-*p*-toluidine.

This paper presents the results of experiments in which di-*p*-toluidinomethane, methylene-*p*-toluidine and di-*p*-phenetidinomethane were treated in varying proportions and under various conditions with the corresponding amine and amine salt. Fifty to ninety per cent. of the starting materials were accounted for by the formation of di- and tetrahydroquinazolines, aminobenzylaniline bases, amines (toluidine or phenetidine) and methylated amines (methyltoluidine or methylphenetidine).

The formation of quinazolines and the occurrence of methylation during interaction of para substituted primary aromatic amines and formaldehyde in wholly or partially aqueous media containing acid has been reported by Maffei,[8] by Eisner and Wagner,[9] by Wagner,[10] and by Cairncross and Bogert.[11] Several of these investigators have discussed the mechanism of heterocycle formation and of methylation.[8c,9,10] The initial product is the diimine (or Schiff base) which rearranges to the aminobenzylaniline base. From this the several obtainable heterocyclic compounds are formed owing to the reactivity of the system



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[1] Present address, Mellon Institute of Industrial Research, Pittsburgh, Pa.

[2] See Wagner, THIS JOURNAL, **55**, 724 (1933), for leading references.

[3] Wagner, *ibid.*, **56**, 1944 (1934).

[4] German patent 105,797, *Frdl.*, **5**, 84; 87,934, *Frdl.*, **4**, 66.

[5] German patent, 53,937, *Frdl.*, **2**, 53.

[6] German patent, 55,848, *Ber.*, **24**, ref. 504 (1891).

[7] This change is superficially a two stage isomerization and is often referred to as a rearrangement [(a) Moore and Johnson, THIS JOURNAL, **57**, 1517 (1935); (b) Braun and Kruber, *Ber.*, **45**, 2977 (1912); (c) Cohn and Fischer, *ibid.*, **33**, 2586 (1900); (d) Meyer and Rohmer, *ibid.*, **33**, 250 (1900); (e) Eberhardt and Welter, *ibid.*, **27**, 1804 (1894)]. Actually it is a fission and coupling, for by interaction of a base, its hydrochloride and the aminobenzylaniline base from a different amine there results a diphenylmethane base of "mixed" type.[c]

[8] (a) Lepetit and Maimeri, *Atti accad. Lincei*, [5] **26**, 558 (1917); (b) Lepetit, Maffei and Maimeri, *Gazz. chim. ital.*, **57**, 867 (1927); (c) Maffei, *ibid.*, **58**, 261 (1928).

[9] Eisner and Wagner, THIS JOURNAL, **56**, 1938 (1934).

[10] Wagner, *ibid.*, **57**, 1296 (1935).

[11] Cairncross and Bogert, *Collection Czechoslov. Chem. Communications*, **7**, 548 (1935); **8**, 57 (1936).

whose two amino groups are suitably disposed to permit ring closure with formic acid or formaldehyde. In these reactions the formaldehyde and formic acid needed to effect ring closure are demonstrably present so that formation of quinazolines is readily explicable. In the experiments recorded below, however, no such agents are present, the conditions being in fact those previously considered suitable for the formation of aminobenzylaniline and diphenylmethane bases. It was therefore necessary to determine the manner in which the diimine or Schiff base, by the action of amine hydrochloride and amine, yields (through the aminobenzylaniline base) the tetrahydroquinazoline, the dihydroquinazoline and methylated amine.

The probable course of the formation of such compounds from *o*-amino-*m*-xylyl-*p*-toluidine is indicated in Fig. 1.

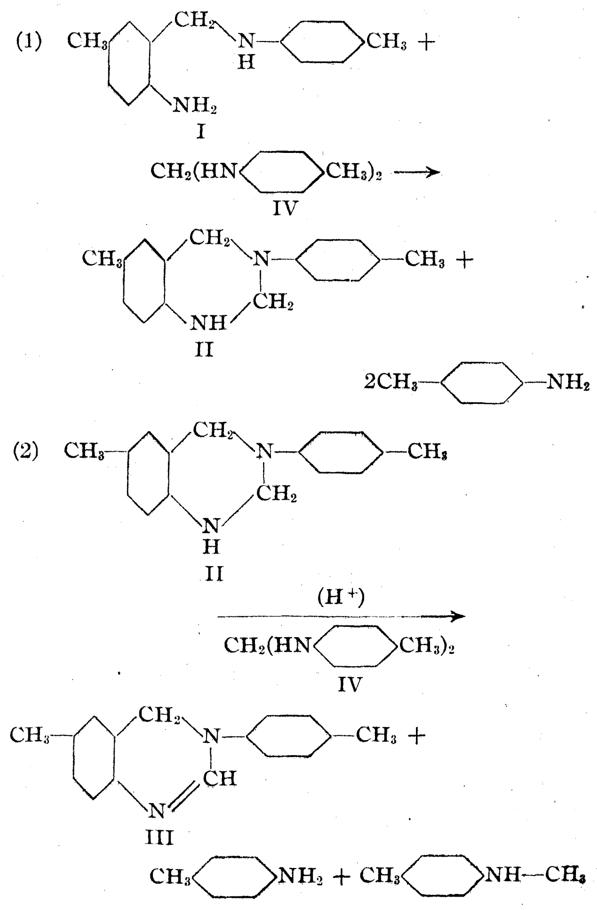
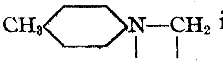


Fig. 1.

Reaction 1 has been realized independently in the present study. It is the counterpart of the formation of II from I and formaldehyde,[12] both reactions occurring in the absence of acids. The fact that II can also be formed by the action of formaldehyde in the presence of free acid in the cold as shown by Wagner[13] removes any doubt that the same compound may result by reaction 1, in the presence of amine salt. It is to be considered probable, however (see below), that under such conditions the reaction may be reversible.

Evidence for reaction 2, the conversion of II to III, is less direct but is circumstantially convincing. The data from experiments in which quinazolines are formed from IV show that conditions which lead to an increased yield of II bring about an approximately corresponding decrease in the yield of III and *vice versa*. This seems to indicate that the tetrahydro is a precursor of the dihydroquinazoline. The formation of III would accordingly require the dehydrogenation of II by some suitable hydrogen acceptor. Removal by conventional means of the two hydrogens involved was effected by mild oxidation with permanganate in acetone solution.[14] It is suggested that in the conversions of diimine reported in this paper the tetrahydro compound is "oxidized" by the diimine in the presence of amine salt or the fragment . As a result of such a reaction methyl-*p*-toluidine is formed. This is supported by the experimental fact that only when III was formed was there any secondary amine among the reaction products. It appears impossible to devise an experiment to test the "oxidation" of II by diimine because the diimine can only produce the fragment  in the presence of an amine salt (or acid) which was found independently to bring about a conversion of II to III.

Thus heating together II and *p*-toluidine hydrochloride produced III, methyl-*p*-toluidine and 2,2′-diamino-5,5′-dimethyldiphenylmethane. These results serve to (1) illustrate the unusual properties of the tetrahydroquinazoline and (2) support the idea of its "oxidation" by the diimine. The appearance of the diphenylmethane base suggests the intermediate formation of I by a cleavage of the tetrahydroquinazoline ring by the action of amine salt

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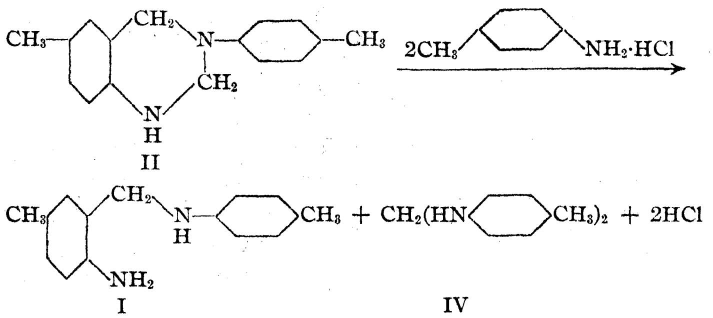
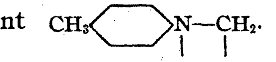
(12) Ref. 9, p. 1942.

(13) Ref. 10, p. 1297.

(14) German patent 92,084, *Frdl.*, **4**, 131.



A similar cleavage of tetrahydroquinazolines in aqueous acids produces aminobenzylamines and aldehydes.[15] Benzoyl chloride in pyridine also brings about fission,[16] compound II yielding the benzoyl derivative of I. Toluidine hydrochloride, however, produces IV in addition to I so that the cleavage is actually reaction 1 reversed by the presence of amine salt. The diimine in the presence of the hydrochloride cleaves to toluidine and the fragment  Aminoxylyltoluidine by the action of toluidine and toluidine hydrochloride is converted to the diphenylmethane base.[3] The fragment  now "oxidizes" uncleaved II, being itself reduced to methyltoluidine. In this respect the reaction would be analogous to the Doebner reaction in which secondary amine is produced from a dihydrocinchoninic acid and a methylene amine ArCH=NAr.[17] The quantities of toluidine and methyltoluidine formed during the conversions of IV to III and II were observed experimentally to be in roughly quantitative agreement with the requirements of the reactions in Fig. 1. From these considerations it seems certain that in the conversion of IV to III methylation occurs during the conversion of the intermediately formed tetrahydroquinazoline to the dihydroquinazoline and that formation of the latter involves the "oxidation" of the tetrahydroquinazoline by di-*p*-toluidinomethane or the fragment 

A similar series of reactions explains the conversion of di-*p*-phenetidinomethane to 3-*p*-phenetyl-6-ethoxy-3,4-dihydroquinazoline and methyl-*p*-phenetidine.

Experimental Part

Preparation of Materials.—Di-*p*-toluidinomethane, m. p. 95.5–96.0° corr., was prepared according to Eberhardt and Welter;[18] di-*p*-phenetidinomethane, m. p. 80.3–81.0° corr. by the directions of Bischoff.[19] *p*-Toluidine and *p*-phenetidine hydrochlorides were crystallized from aqueous solutions by addition of strong hydrochloric acid. 3-*p*-Tolyl-6-methyl-3,4-dihydroquinazoline hydrochloride was prepared by chilling the hot solution of the base in 1:1 hydrochloric acid. It was crystallized from dilute acid, m. p. 219.5° obsd. (226.3° corr.). *p*-Toluidine was Eastman best grade; *p*-phenetidine was vacuum distilled before use. All melting points are corrected.

Rearrangements of Di-*p*-toluidinomethane (IV); General Procedure.—Compound IV (0.01 mole) was mixed with the desired quantities of amine and amine hydrochloride, heated for one-half to four hours at the required temperature, made alkaline and steam distilled.

The steam distillate, in experiments recorded in Table II, was then treated with benzene sulfonyl chloride by the Hinsberg–Kessler procedure to estimate quantities of primary and secondary amines.[20] No tertiary amine was found in these distillates. In some experiments (Nos. 34, 34R, 35, 36, 39) in which small quantities of base hydrochloride were used, preceding the Hinsberg separation the steam distillate was titrated with 0.5 *N* hydrochloric acid using Congo paper as indicator. This served not only as a check on the Hinsberg analysis but to separate primary and secondary amine from unreacted IV which under these conditions was not titratable and could be filtered from the solution of base hydrochloride. A test titration of 1.60 g. of *p*-toluidine in the presence of 0.8 g. of IV indicated 1.62 g. of *p*-toluidine.

Yields of I and III in the non-steam-volatile residue were estimated as follows.

The residue, separated from the alkaline solution by ether extraction or filtration, was dissolved in boiling alcohol (25–50 cc.) and benzaldehyde (1.5–2.0 cc.) added to the hot solution which was kept hot for two to three minutes. On cooling, the benzal derivative of I crystallized. The melting point of this material was usually 127°.[21] The filtrate was then heated to boiling and a solution of picric acid (0.2–0.8 g.) in alcohol (10–15 cc.) added. The picrate of III crystallized on chilling. It melted usually at 210°.[22] A test of this separation of I and III was made with 1.0 g. of I and 0.5 g. of III. The benzal compound weighed 1.24 g., 89.6%; the picrate, 1.07 g., 108%.

An over-all test of the steam distillation, ether extraction and separation using known quantities of I, III, *p*-toluidine and *p*-toluidine hydrochloride and correcting for an 89.6% recovery of I indicated 102% of I and 122% of III.

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(15) Wolff, *Ber.*, **25**, 3033–4 (1892); Busch, *J. prakt. Chem.*, [2] **52**, 413 (1895); [2] **53**, 421 (1896).

(16) Heller, *Ber.*, **37**, 3114, 3118 (1904).

(17) Robinson and Bogert, *J. Org. Chem.*, **1**, 72 (1936); Ciusa and Musajo, *Gazz. chim. ital.*, **59**, 798 (1929); Carrara, *ibid.*, **61**, 625 (1931).

(18) Eberhardt and Welter, Ref. (7e), p. 1808.

(19) Bischoff, *Ber.*, **31**, 3244–3245 (1898).

(20) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, Vol. II, 1916, p. 24.

(21) Von Walther and Bamberg, *J. prakt. Chem.*, [2] **71**, 157 (1905).

(22) Eisner and Wagner, Ref. 9, p. 1940.

To estimate II this procedure had to be modified by extracting I and III from the ether solution of the residue with 0.5 *N* acid. The ether soluble portion on crystallization from ligroin (b. p. 70–90°) yielded II, m. p. 140°.[23]

The identity of III was shown by mixed melting point tests of base and/or picrate with authentic specimens. Compound I was identified by the recovery as its benzal derivative. No derivatives of II were available and its identification consisted in satisfactory mixed melting point determinations. Results are collected in Tables I, II, III.

Rearrangement of Di-*p*-phenetidinomethane.—The diarylaminomethane (5.8 g., 0.02 mole) was heated for four hours on the boiling water-bath with 1.73 g. (0.01 mole) of *p*-phenetidine hydrochloride. The mixture was then made alkaline, steam distilled and the solid, non-volatile residue crystallized once from alcohol yielding 1.17 g. of a slightly yellow product, m. p. 141–142°.[24] The mother liquors gave no precipitate with benzaldehyde showing the absence of aminobenzylaniline base. The benzaldehyde was then removed by steam distillation and the residue converted to an impure picrate, m. p. 140–60°. This on recrystallization from alcohol yielded 0.58 g., m. p. 160–70°. Total yield of 3-*p*-phenetyl-6-ethoxy-3,4-dihydroquinazoline was 1.5 g. (76%).

The steam distillate yielded the benzene sulfonyl derivatives of methyl-*p*-phenetidine, m. p. 65°, and of *p*-phenetidine, m. p. 142–143°.

A second trial of the same procedure with 20 g. (0.07 mole) of the diimine and 3.0 g. (0.01 mole) of the hydrochloride yielded 3.57 g. (52%) of the dihydroquinazoline (2.49 g. of free base, m. p. 140–141°; 1.9 g. of the picrate, m. p. 180–183°).

The following derivatives of phenetylethoxydihydroquinazoline were prepared.

Hydrochloride, by dissolving the base in hot dilute (1:1) acid containing a little alcohol and chilling. The product after recrystallization from dilute acid containing alcohol melted at 195.3°. The reported m. p. is 193°.[24b]

Tetrahydroquinazoline.—Reduction of the dihydro base in alcohol with 9 times the theoretical amount of sodium gave a crude product, m. p. 131–135°. One crystallization from alcohol raised the m. p. to 143–143.5°. (Mixed with the dihydro compound melting at 141–142° the m. p. was 134–135.5°.) Another crystallization yielded pure tetrahydroquinazoline, m. p. 144–144.5°. The reported m. p. is 144°.[24a]

3-*p*-Tolyl-6-methyl-3,4-dihydroquinazoline from Methylene-*p*-toluidine.—Six grams of methylene-*p*-toluidine, 5.8 g. of *p*-toluidine, and 2.9 g. of *p*-toluidine hydrochloride were heated together at 90° for five hours. The non-steam volatile residue was crystallized twice from ligroin (b. p. 90–120°) to give 0.7 g. of III m. p. 163°. From the mother liquors there was isolated a little more of III and some I, m. p. 82°.

3-*p*-Tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline: Interaction of *o*-Amino-*m*-xylyl-*p*-toluidine and Di-*p*-toluidinomethane.[25]—A solution of IV (2.1 g.) and I (2.1 g.) in 90 cc. of alcohol was refluxed for one hour. Eighty cc. of alcohol was then distilled off and the residue allowed to crystallize. The mother liquors were diluted with water, ether was added followed by dilute hydrochloric acid (1:20) to separate toluidine and II. The solute in the ether layer was combined with the first crop of solid and crystallized from ligroin (90–120°) yielding II, m. p. 141°; yield 1.90 g., 86.3%.

The toluidine in the acid layer was recovered as the benzoyl derivative, m. p. 156°; yield 2.1 g., 60.5%.

Oxidation to the Dihydroquinazoline

Action of *p*-Toluidine Hydrochloride.—Compound II (1.19 g., 0.005 mole) and *p*-toluidine hydrochloride (1.6 g., 0.011 mole) in 50 cc. of alcohol were refluxed four hours. The products were isolated by the usual procedure. The benzal derivative weighed 0.12 g., melted at 182–184.5° and proved to be 2,2-dibenzalamino-5,5′-dimethyldiphenylmethane by mixed melting point of 183.5° with a specimen prepared as described below and melting at 186°. The yields of other products were: III, 0.40 g.; methyl-*p*-toluidine, 0.11 g.; *p*-toluidine, 0.83 g.

A duplicate experiment run at 110° for two hours without alcohol and worked up in the same way gave essentially the same yields of the same products.

Permanganate Oxidation.—Seventy-five cc. of acetone containing 0.63 g. of potassium permanganate was added in portions to II (1.19 g.), dissolved in 75 cc. of acetone. The reaction took place immediately and was allowed to proceed at room temperature. The precipitated manganese dioxide was filtered off and the product in the filtrate converted to the picrate as usual. The yield was 28.8% of picrate which after crystallization from alcohol melted at 208–209°.

Action of Di-*p*-toluidinomethane and *p*-Toluidine Hydrochloride.—A mixture of IV and II (1.2 g. each) was heated with 1.6 g. of *p*-toluidine hydrochloride in 50 cc. of alcohol for three hours at 61 ± 1°. The yields were: I, 0.36 g.; III, 0.40 g.; methyl-*p*-toluidine, 0.26 g.; *p*-toluidine, 1.44 g. These data indicate that 0.84 g. of IV was available to take part in reactions forming 0.40 g. of III. The ratio of 3 diimine to 1 of III indicates, however, that only 0.29 g. of III could be formed from this quantity of available IV. It may be concluded that 0.11 g. of III was formed from II.

Cleavage by Benzoyl Chloride.—One gram of II was treated in benzene solution with 2 cc. of pyridine and 1.0 cc. of benzoyl chloride. Recovery of the benzoylation product in the ordinary manner[26] yielded, after one crystallization, 0.45 g. of white crystalline material melting at 186–190°. Recrystallization from dilute alcohol gave a product melting at 190.2–190.5°. This material was identical with a sample melting at 188.5–189° prepared from II by the usual Schotten–Baumann procedure as shown by a mixed m. p. of 189°. Benzoylation of I in aqueous alkali gave the same compound, m. p. 189.6°, mixed m. p. 190°, shown by analysis to be the dibenzoyl derivative of I and not the monobenzoyl derivative.

Anal. Calcd. for $C_{29}H_{26}N_2O_2$: N, 6.45. Found: N, 6.50.

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[23] Von Walther and Bamberg, *J. prakt. Chem.*, [2] **73**, 209 (1906).

[24] (a) Maffei, *Gazz. chim. ital.*, **59**, 3–9 (1929); (b) Goldschmidt, *Chem.-Ztg.*, **21**, 395 (1897).

[25] Thanks are due Mr. S. A. Shrager for carrying out this experiment.

[26] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1935, p. 146.

2,2'-Dibenzalamino-5,5'-dimethyldiphenylmethane.—The diphenylmethane base (0.24 g., 0.01 mole) in 5 cc. of alcohol was treated in the hot with 0.22 g. (0.02 mole) freshly distilled benzaldehyde. The solution was boiled for a few minutes and then chilled to give 0.38 g. of a product melting at 182–184°. One crystallization from alcohol gave the pure derivative with m. p. 186°. Analysis showed it to be a dibenzal derivative.

Anal. Calcd. for $C_{29}H_{26}N_2$: N, 6.97. Found: N, 6.98.

Discussion of Results

Formation of *o*-Amino-*m*-xylyl-*p*-toluidine.—The data of a number of experiments performed to ascertain the effect of conditions on the production of this base from di-*p*-toluidinomethane are tabulated in Table I. The largest yield was 82.5% obtained by using a molar ratio of diimine: toluidine hydrochloride: toluidine of 1:1:25. The data showed that (1) the time required for reaction was not more than one-half hour, longer periods of heating had no beneficial effect; (2) the temperature at which the reaction proceeded within the limits of 60 and 100° had no effect on the yields; (3) the effect of solvent (alcohol) was to lower the yield of I and increase the quantity of III; (4) the amount of toluidine hydrochloride had to be greater than 0.01 g. (0.0001 mole) for 2.26 g. (0.01 mole) of diimine in order for any transformation to take place; (5) the best conversions were observed when there was used 0.005–0.01 mole of hydrochloride per 0.01 mole of diimine; 0.001 mole of hydrochloride resulted in smaller yields of I, larger yields of III and the formation of II.

Formation of Quinazolines.—A number of experiments were made to find out under what conditions these compounds became the major products of the transformation of IV. The data are recorded in Table II. In the absence of a solvent the greatest amount of III obtained was 0.00144 mole from 0.01 mole of diimine (43.2%). This quantity resulted when only diimine and toluidine hydrochloride reacted and was essentially the same as long as the molar ratio of hydrochloride:diimine remained larger than 0.5. When less hydrochloride was used the yield of III decreased and II was found among the products. Compound I was found under practically all conditions (up to 0.0023 mole). When alcohol was used as a solvent the quantity of III was raised to 0.0021–0.0025 mole (62–75%) while the amount of I was lowered to 0.0005 mole or less. In all of these experiments both methyl-*p*-toluidine and *p*-toluidine were produced.

In Table III are recorded the yields of III obtained from the diimine by the action of a number

TABLE I

CONVERSION OF DI-*p*-TOLUIDINOMETHANE TO *o*-AMINO-*m*-XYLYL-*p*-TOLUIDINE

EFFECT OF CONDITIONS: (10 mmol. (2.26–2.3 g.) diimine used in each expt.). EFFECT OF TIME, TEMPERATURE, AND SOLVENT: (50 mmol. (5.5 g.) *p*-toluidine; 5 mmol. (0.7 g.) *p*-toluidine hydrochloride).

Expt.	17	18	19	20	21	20A	15
Conditions							
Hrs. htd.	4	3	3	3	3	0.5	3
Temp., ° C.	60 ± 5	60 ± 1	70 ± 1	80 ± 1	90 ± 1	85 ± 5	78–80
Solvent	...	...	...	...	...	...	Alc. (50 cc.)
Products							
I, mmol.	7.43	7.19	6.90	6.86	6.72	6.77	4.12
III, mmol.	0.51	0.64	0.68	0.64	0.76	0.42	1.48
Total mmol. diimine acctd. for	8.96	9.09	8.94	8.78	9.00	8.03	8.56

EFFECT OF RATIO, *p*-TOLUIDINE: *p*-TOLUIDINE HYDROCHLORIDE

Temp. 80–90°, No Solvent

Expt.	20A	43	20B	13	44	46	48
Conditions							
p-Tol., mmol.	50	50	50	50	50	250	10
p-T. HCl, mmol.	5	1	0.1	0.0	10	10	10
Molar ratio	10	50	500		5	25	1
Products							
I, mmol.	6.77	3.58	0.0	0.0	6.15	8.24	2.28
III, mmol.	0.42	0.68	0.0	0.0	0.64	0.25	1.40
Total mmol. diimine acctd. for	8.03	5.62	...	...	8.07	9.00	6.48

TABLE II

CONVERSION OF DI-*p*-TOLUIDINOMETHANE TO 3-*p*-TOLYL-6-METHYL-3,4-DIHYDROQUINAZOLINE
(10 mml. (2.26–2.3 g.) diimine used in each expt.)

Expt.	25	16	10C	10A	35	34	34R	36	39
Reagents									
p-Tol. HCl, mmol.	10	5	10	5	5	1	1	0.5	0.1
Solvent	Alc. (50 cc.)	Alc. (50 cc.)	..	..	..	..	..	..	...
Products									
I, mmol.	0.50	0.00	2.30	2.30	2.30	0.25	0.14	0.0	[a]
III, mmol.	2.08	2.50	1.33	1.35	1.44	1.14	0.98	0.85	...
II, mmol.	[b]	[b]	[b]	[b]	[b]	0.84	0.55	0.01	...
p-Tol., mmol.	4.6	..	[b]	2.15[c]	[b]	7.19	7.96	8.40	...
Me-*p*-Tol., mmol.	[b]	[b]	[b]	[d]	0.69	0.96	1.03	0.77	...

[a] About 15% of unreacted diimine recovered from steam distillate. [b] Not determined. [c] Determined in a duplicate experiment. [d] Identified but not determined.

of different salts. The hydrochloride of III gave the largest yield in these trials. Small yields were obtained by the action of ammonium chloride and dimethylaniline hydrochloride. Zinc chloride yielded none of III.

TABLE III

CONVERSION OF DI-*p*-TOLUIDINOMETHANE TO 3-*p*-TOLYL-6-METHYL-3,4-DIHYDROQUINAZOLINE

(10 mml. of di-*p*-toluidinomethane and various salts as catalysts; no solvent

Expt.	Salt	Mml.	Mml. III
14	$ZnCl_2$	2.0	0.0[a,b]
28	Dimethylaniline hydrochloride	10.0	0.77[a,c]
29	Hydrochl. of III	1.0	1.86[a]
45	NH_4Cl	10.0	0.77[a]
34	*p*-Tol. HCl	1.0	1.14[a]

[a] No attempt made to isolate compd. II. [b] Isolated 0.18 g. subs. m. p. 227–230° obsd. not identified. [c] Major product was tetramethyldiaminodiphenylmethane, m. p. 87°.

Summary

1. Di-*p*-toluidinomethane by the action of *p*-toluidine and *p*-toluidine hydrochloride has been shown to yield *o*-amino-*m*-xylyl-*p*-toluidine, 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline, 3-*p*-tolyl-6-methyl-3,4-dihydroquinazoline, *p*-toluidine and methyl-*p*-toluidine.

2. This conversion has been studied using varying proportions of reactants and under a variety of conditions essentially those previously thought suitable for converting di-*p*-toluidinomethane to *o*-amino-*m*-xylyl-*p*-toluidine or 2,2′-diamino-5,5′-dimethyldiphenylmethane.

3. Di-*p*-phenetidinomethane similarly yielded 3-*p*-phenetyl-6-ethoxy-3,5-dihydroquinazoline and methyl-*p*-phenetidine.

4. The probable course of the formation of quinazolines under these conditions has been shown to consist in the intermediate production of a tetrahydroquinazoline from the aminobenzylaniline base followed by "oxidation" to a dihydroquinazoline effected by the diarylaminomethane in an acid medium.

5. The interaction of di-*p*-toluidinomethane and *o*-amino-*m*-xylyl-*p*-toluidine to yield 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline and its behavior toward a number of reagents has been described.

PHILADELPHIA, PENNA. RECEIVED DECEMBER 24, 1936

[CONTRIBUTION FROM NICHOLS LABORATORY OF NEW YORK UNIVERSITY]

Condensation Reactions of Quinoline Aldehydes

BY CHARLES E. KWARTLER[1] AND H. G. LINDWALL

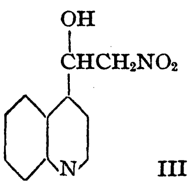
It has been found that lepidine and 6-methoxylepidine yield the corresponding quinoline-4-aldehydes when subjected to oxidation through the action of selenium dioxide. Their behavior with that oxidizing agent is analogous to that of quinaldine, which, as has been reported, is converted to quinoline-2-aldehyde.[2]

Quinoline-4-aldehyde (I) was isolated from its reaction mixture by steam distillation as the hydrate, which loses water upon being recrystallized from absolute toluene, or after long standing in a vacuum desiccator over sulfuric acid. Compound I reduces Tollens' reagent, and forms a sodium bisulfite addition product slowly; it has been characterized by oxime formation and by the preparation of its *p*-nitrophenylhydrazone.

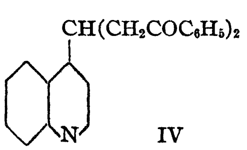
It was found that 6-methoxyquinoline-4-aldehyde (II) does not steam distil; it was isolated directly from the reaction mixture as the free aldehyde. Even after crystallization from water no hydrate was obtained. Compound II reduces Tollens' reagent, and forms an oxime. The corresponding cinchoninic acid is a by-product in the preparation of both I and II.

Quinoline-4-aldehyde hydrate melts at 84–84.5°, and the free aldehyde (I) at 51–53°. Neither of these melting points agrees with that (101–102°) reported by Koenigs[3] for the oxidation product of apocinchene, for which he suggested the quinoline-4-aldehyde structure.

Quinoline-4-aldehyde hydrate (I) condenses with nitromethane, yielding β-hydroxy-β-(quinolyl-4)-α-nitroethane (III). This reaction is catalyzed by diethylamine. Condensation of acetophenone with I takes place in the presence of sodium hydroxide; the product is diacetophenonyl-lepidine (IV). Compound IV forms a dioxime with hydroxylamine.

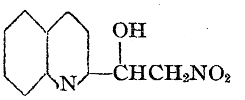


III



IV

Quinoline-2-aldehyde hydrate reacts with "active-methylene" compounds somewhat more readily than does I. Nitromethane, in the presence of diethylamine, condenses to yield β-hydroxy-β-(quinolyl-2)-α-nitroethane (V). Acetophenone likewise yields an aldol-like product, (VI) β-hydroxy-β-(quinolyl-2)-ethyl phenyl ketone, when either diethylamine or sodium hydroxide is used as the catalyst.



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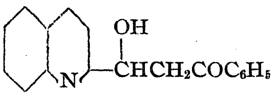
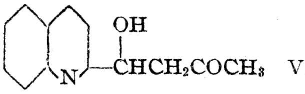
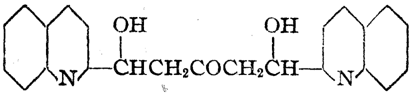


VI

The action of acetone with quinoline-2-aldehyde hydrate also has been studied. Two products result, depending upon the conditions (described in the Experimental part) under which the reactions are carried out. These condensation products are of the aldol type, 4-hydroxy-4-(quinolyl-2)-butanone-2 (VII) and 1,5-dihydroxy-1,5-bis-(quinolyl-2)-pentanone-3 (VIII).



VII



VIII

This research is being continued with the study of further condensation reactions, and their products, especially in the case of quinoline-4-aldehyde and its 6-methoxy derivative.

Experimental Part

Hydrate of Quinoline-4-aldehyde (I).—4-Methylquinoline (4 g.) was dissolved in 60 cc. of xylene, and the solution was held at 135° with constant stirring. Selenium dioxide (4.5 g.) was added in small portions over the period of one-half hour, after which the mixture was held at 135° for one hour. As selenium formed the mixture gradually became dark red. Upon cooling, crystals of cinchoninic acid separated; this and selenium were removed by filtration. The filtrate was steam distilled and the aldehyde collected separately after the xylene had distilled. The hydrate of I was filtered from the distillate after standing overnight, and more was obtained from the ether extract of the dis-

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(1) From the dissertation presented by Charles E. Kwartler to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy.

(2) Monti, *Atti accad. Lincei*, **18**, 505 (1933); Henze, *Ber.*, **67**, 750 (1934).

(3) Koenigs, *J. prakt. Chem.*, **61**, 23 (1900).

tillate; yield, 61%, of small plates, m. p. 84–84.5°, soluble in water, toluene, xylene, ether, ethyl alcohol.

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.57; H, 5.15; N, 8.00; mol. wt., 175. Found: C, 68.77, 68.89; H, 5.02, 5.03; N, 7.86, 7.71; mol. wt., 174, 174.

Quinoline-4-aldehyde (I).—The hydrate of I formed I after three weeks in a vacuum desiccator, or upon recrystallization from absolute toluene as colorless needles, m. p. 51–53°; these are soluble in ether, butyl alcohol, toluene, xylene. Compound I gives a positive reaction with Tollens' reagent, and forms a sodium bisulfite addition product slowly.

Anal. Calcd. for $C_{10}H_7NO$: N, 8.92. Found: N, 8.93.

Cinchoninic Acid.—4-Methylquinoline with larger amounts of selenium dioxide, and with longer heating of the mixture than described above for the preparation of I, is oxidized to cinchoninic acid in excellent yields.

***p*-Nitrophenylhydrazone of I.**—Yellow rectangular prisms from ethyl alcohol, m. p. 261–262°. Slightly soluble in warm carbon tetrachloride.

Anal. Calcd. for $C_{16}H_{12}O_2N_4$: N, 19.18. Found: N, 19.16.

Oxime of I.—White needles from methyl alcohol, m. p. 181–182°; yield, 88%.

Anal. Calcd. for $C_{10}H_8ON_2$: N, 16.28. Found: N, 16.33, 16.41.

6-Methoxyquinoline-4-aldehyde (II).—Compound II was prepared by the oxidation of 6-methoxy-4-methylquinoline in a manner identical with that employed for the preparation of the hydrate of I. Upon attempted steam distillation of the reaction mixture it was found that none of II would distil, and it was isolated from the residual material after steam distillation of the xylene. No hydrate was obtained even after crystallization from water: needles, m. p. 96–98°, from toluene; soluble in water, ethyl alcohol, xylene; reduces Tollens' reagent; yield, 52%.

Anal. Calcd. for $C_{11}H_9NO_2$: N, 7.49. Found: N, 7.49.

Oxime of II. Needles from ethyl alcohol; m. p. 214–216°; soluble in toluene.

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: N, 13.86. Found: N, 13.81.

Oxime of Quinoline-2-aldehyde.—Fine white needles from 80% ethyl alcohol. The melting point of this compound, 188–190°, prepared by the action of hydroxylamine with quinoline-2-aldehyde, is in agreement with that reported by Pfitzinger,[4] who prepared this oxime by another method.

2′,4′ - Dinitrophenylhydrazone of Quinoline - 2 - aldehyde.—Yellow needles were obtained by diluting the ethyl alcohol solution of the crude product with water to incipient crystallization and allowing the mixture to stand, m. p. 251–253°.

Anal. Calcd. for $C_{16}H_{11}O_4N_5$: N, 20.59. Found: N, 20.77.

β - Hydroxy - β - (quinolyl - 4) - α - nitroethane (III).—A mixture of 0.3 g. of nitromethane, 0.5 cc. of absolute alcohol and 2 drops of diethylamine was cooled in ice and to it was added 0.32 g. of the hydrate of I. The reaction mixture was held at room temperature for one day, and then the alcohol was allowed to evaporate partially. Compound III separated as small plates, soluble in toluene, acetic acid and ethyl alcohol; recrystallized from ethyl alcohol, m. p. 133–136°; yield 78%.

Anal. Calcd. for $C_{11}H_{10}O_3N_2$: N, 12.84. Found: N, 12.50.

β - Hydroxy - β - (quinolyl - 2) - α - nitroethane (V).—A mixture was prepared of quinoline-2-aldehyde hydrate (0.43 g.) and 2 drops of diethylamine; to this was added 0.34 g. of nitromethane and 0.5 cc. of absolute ethyl alcohol. The reaction mixture became warm. Upon cooling, V separated as long white needles from ethyl alcohol; m. p. 110–113°; soluble in ethyl alcohol, isopropyl alcohol and acetic acid; yield 81%.

Anal. Calcd. for $C_{11}H_{10}O_3N_2$: N, 12.84. Found: N, 12.54.

Diacetophenonyl-lepidine (IV).—To a mixture of 6 cc. of 10% sodium hydroxide and 15 cc. of 95% ethyl alcohol were added 0.35 g. of acetophenone, 0.25 g. of the hydrate of I, and some small chips of ice. The temperature of the reaction mixture was allowed to rise to that of the room, and after one-half hour IV began to separate as white needles. Recrystallized by the slow dilution of the ethyl alcohol solution with water; yield 87%; m. p. 144–146°. Slight variations in the conditions for condensation resulted in other products which have not been studied.

Anal. Calcd. for $C_{26}H_{21}O_2N$: N, 3.69. Found: N, 3.52, 3.74.

Dioxime of IV.—Colorless needles from a methyl alcohol and dioxane mixture; m. p. 204–205°.

Anal. Calcd. for $C_{26}H_{23}O_2N_3$: N, 10.27. Found: N, 10.39.

β-Hydroxy-β-(quinolyl-2)-ethyl Phenyl Ketone (VI). Method A.—To a 10% solution of sodium hydroxide (15 cc.) were added 8 cc. of 95% ethyl alcohol, 0.2 g. of acetophenone, 0.2 g. of quinoline-2-aldehyde hydrate and a few chips of ice. Soon a light yellow solid (VI) separated and was recrystallized by the careful addition of water to its alcohol solution as pale yellow needles, m. p. 114–116°; yield 78%. **Method B.**—A solution of 0.12 g. of quinoline-2-aldehyde hydrate and 0.12 g. of acetophenone in 8 cc. of absolute ethyl alcohol was cooled in ice, and to it was added 2 drops of diethylamine. After four days water was added, and VI precipitated; purified as above in method A; yield 77%.

Anal. Calcd. for $C_{18}H_{15}O_2N$: N, 5.05. Found: N, 4.94, 4.99, 5.04.

4 - Hydroxy - 4 - (quinolyl - 2) - butanone - 2 (VII).—To a solution consisting of 12 cc. of 10% aqueous sodium hydroxide and 10 cc. of 95% ethyl alcohol were added 0.11 g. of quinoline-2-aldehyde hydrate, 0.15 g. of acetone and a few small chips of ice. Turbidity resulted after a few minutes of shaking, and soon VII separated in 68% yield. It was recrystallized from ethyl alcohol; m. p. 164–167°.

Anal. Calcd. for $C_{13}H_{13}O_2N$: N, 6.51. Found: N, 6.64.

1,5-Dihydroxy-1,5-bis-(quinolyl-2)-pentanone-3 (VIII).—A mixture was prepared consisting of 0.4 cc. of ace-

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[4] Pfitzinger, *J. prakt. Chem.*, **66**, 264 (1902).

tone, 0.9 cc. of 95% ethyl alcohol and 4 drops of diethylamine; to this was added 0.31 g. of quinoline-2-aldehyde hydrate. The reaction mixture was allowed to remain at room temperature for two days, and at the end of that time crystals of VIII had separated: soluble in benzene, xylene, butyl alcohol; recrystallized from xylene; m. p. 208–210°; yield 32%.

Anal. Calcd. for $C_{23}H_{20}O_3N_2$: N, 7.53. Found: N, 7.60.

Summary

Lepidine and 6-methoxylepidine are oxidized by selenium dioxide to quinoline-4-aldehyde and 6-methoxyquinoline-4-aldehyde, respectively. Quinoline-4-aldehyde condenses with nitromethane to give a product of the aldol type, while acetophenone yields diacetophenonyl-lepidine. Quinoline-2-aldehyde, previously described, forms aldol-like products with acetone, acetophenone and nitromethane.

UNIVERSITY HEIGHTS
NEW YORK, N. Y.

RECEIVED JANUARY 18, 1937

[CONTRIBUTION FROM PRIVATE LABORATORIES, AND RESEARCH LABORATORIES, MERCK AND COMPANY, INC.]

Studies of Crystalline Vitamin B_1. XV. C-Methylated 6-Amino- and 6-Oxypyrimidines

BY ROBERT R. WILLIAMS, A. E. RUEHLE AND JACOB FINKELSTEIN

For purposes of comparison with the pyrimidine cleavage products of vitamin B_1 (Aneurin), we have prepared 6-amino- and 6-oxypyrimidine and all of the possible mono- and di-C-methyl derivatives and have observed the ultraviolet absorption of each. 5-ethyl-6-aminopyrimidine is also included. The literature references indicate the methods of preparation of certain known compounds.[1] Some known compounds were obtained by new methods: *e. g.*, 4-methyl-6-oxy- and 5-methyl-6-oxypyrimidines were obtained by oxidizing the 2-thio derivatives with hydrogen peroxide.[2] 2,5-Dimethyl-6-oxypyrimidine resulted from condensing sodioformylpropionic ester with acetamidine and the oxy derivative was converted in the conventional way to the amino. The preparative operations were not carried out repeatedly so the reported yields in general are probably not optimal.

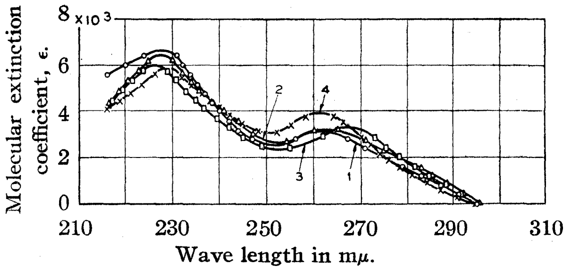

Fig. 1.—1. 6-Oxypyrimidine. 2. 4-Methyl-6-oxypyrimidine. 3. 2-Methyl-6-oxypyrimidine. 4. 5-Methyl-6-oxypyrimidine.

Discussion of Results

Curves of ultraviolet absorption in water solution for the series of 6-oxypyrimidines are shown in Figs. 1, 2 and 3. A great similarity of character is observed throughout, all the compounds exhibiting absorption in two bands which vary somewhat in frequency and slightly in intensity according to the number and position of substituent alkyls. Curves of this character are observed also in other oxy compounds in which one hydrogen of a substituent methyl group is replaced by ethoxy, halogen or sulfonic group as will develop in later papers.

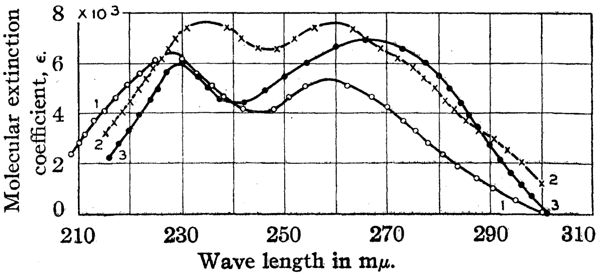

Fig. 2.—1. 2,4-Dimethyl-6-oxypyrimidine. 2. 4,5-Dimethyl-6-oxypyrimidine. 3. 2,5-Dimethyl-6-oxypyrimidine.

The 6-amino series shows a kindred absorption in water solution (Figs. 4 and 5), but the curves are less homogeneous in type than in the oxy series. The amino compounds show a striking

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(1) (a) 6-Oxypyrimidine—Wheeler, *J. Biol. Chem.*, **3**, 287 (1907); (b) 6-aminopyrimidine—Buttner, *Ber.*, **36**, 2232 (1903); (c) 2-methyl-6-oxy- and 2-methyl-6-aminopyrimidine—Gabriel, *ibid.*, **37**, 3638 (1904); (d) 5-ethyl-6-aminopyrimidine—v. Merkatz, *ibid.*, **52**, 871 (1919); (e) 2,4-dimethyl-6-oxypyrimidine—Wollner, *J. prakt. Chem.*, [2] **29**, 132 (1884); (f) 2,4-dimethyl-6-aminopyrimidine—v. Meyer, *ibid.*, [2] **27**, 152 (1883).

(2) Wheeler and McFarland, *Am. Chem. J.*, **42**, 105 (1909).

influence of added acid and alkali as well as a lesser influence of the number and position of substituent alkyl groups. Comparison of each amino derivative with the corresponding oxy compound reveals that the marked acid–alkali contrasts are associated with the presence of the basic amino group (*cf.* Fig. 3 with Figs. 4 and 5).

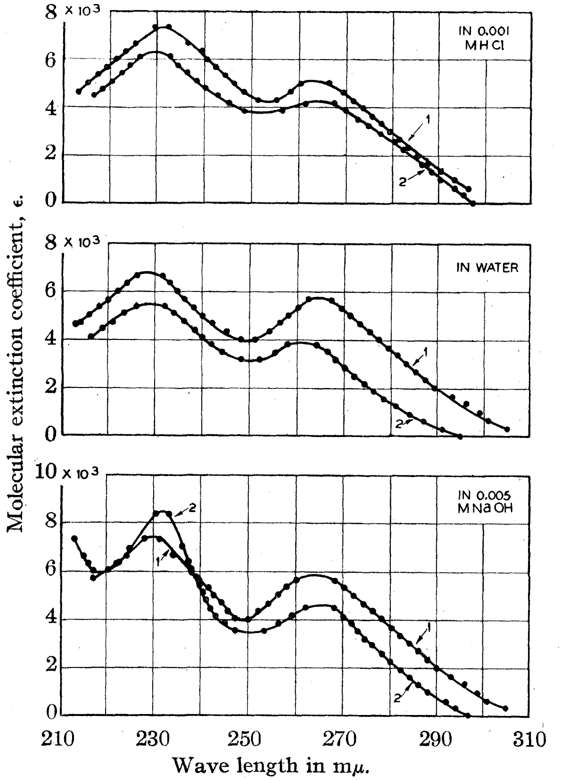

Fig. 3.—(a) In 0.001 *M* HCl, (b) in water, (c) in 0.005 *M* NaOH. 1. 2,5-Dimethyl-6-oxypyrimidine. 2. 5-Methyl-6-oxypyrimidine.

It will be noted that in the absence of added acid or alkali the 6-amino series shows a considerable range in respect to the relative prominence of the two absorption bands and that the addition of alkali in each case tends in the direction of equal prominence of the bands, that of acid toward submerging both bands under a more intense one at about 250 mμ. This fact suggested that the variation exhibited by the series in the absence of added base or acid might be a reflection of the basic strength of the several members of the series. Colorimetric determinations of the *p*H of concentrated water solutions of the compounds (see Table I), however, do not bear out this view in a quantitative sense.

The phenomenon which we have observed may well be intimately related in some fashion to the effect of acid and alkali on guanine,[3] as well as to the effect of acid on the vitamin itself.[4]

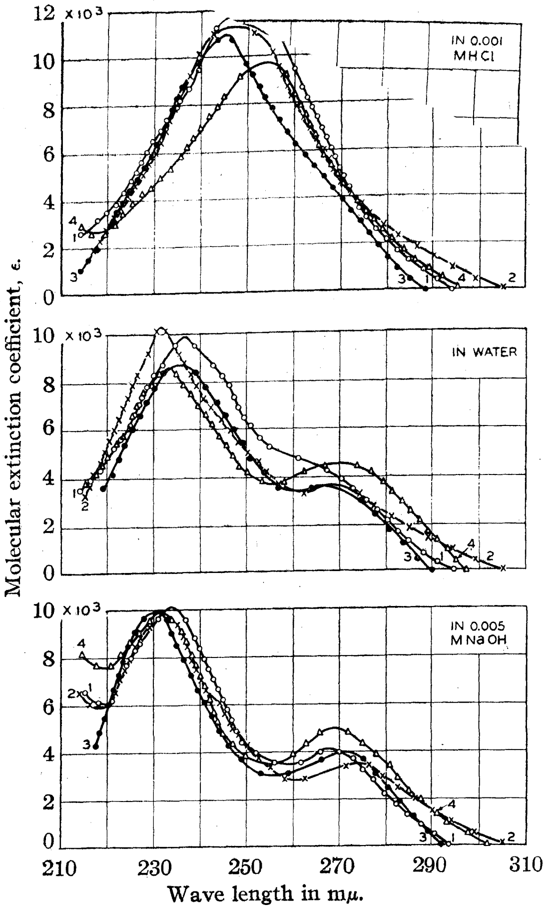

Fig. 4.—(a) In 0.001 *M* HCl, (b) in water, (c) in 0.005 *M* NaOH. 1. 4-Methyl-6-aminopyrimidine. 2. 6-Aminopyrimidine. 3. 2-Methyl-6-aminopyrimidine. 4. 5-Methyl-6-aminopyrimidine.

In the amino as in the oxy series, there is evidence which will be presented at a later time that substituents in side chains do not in general affect absorption profoundly.

It is of interest to note that the amino sulfonic acid, derived from the vitamin, exhibits only an inconspicuous band at 268 mμ in water solution (Fig. 6) which, however, becomes prominent in alkali and then more resembles that of the oxysulfonic acid. This behavior appears quite consistent with that of the 6-aminopyrimidines when one reflects that the acidic character of the sulfonic group would be expected to modify the absorption in the direction of submerging the band at the longer wave length. The weight

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(3) F. F. Heyroth and J. R. Loofbourow, This Journal, **56**, 1728 (1934); Holiday, *Biochem. J.*, **24**, 619 (1930).

(4) Holiday, *ibid.*, **29**, 718 (1935).

of the sulfonic group on the other hand presumably tends to shift this band toward longer wave lengths.

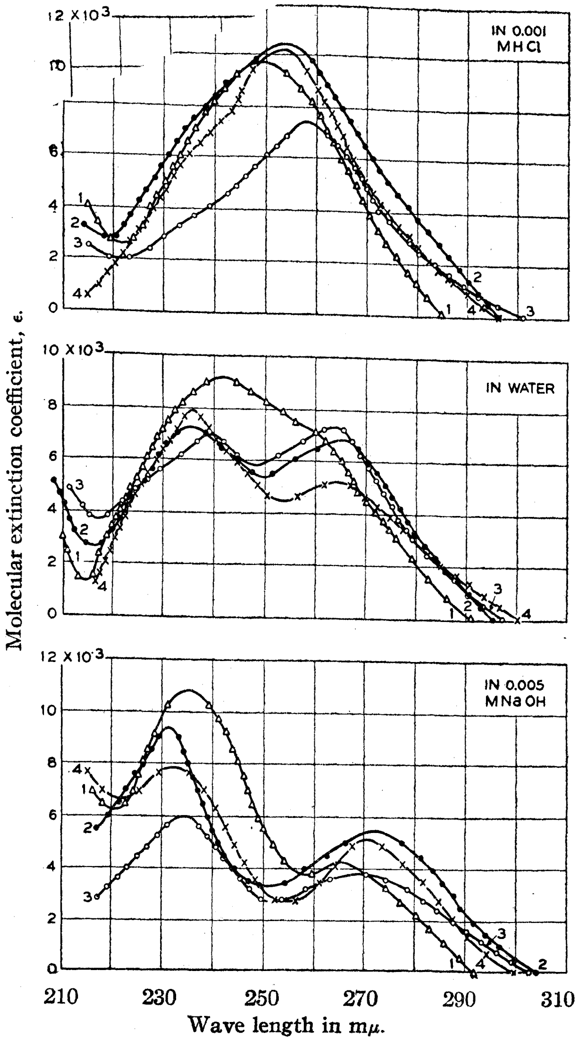

Fig. 5.—(a) In 0.001 M HCl, (b) in water, (c) in 0.005 M NaOH. 1. 2,4-Dimethyl-6-aminopyrimidine. 2. 2,5-Dimethyl-6-aminopyrimidine. 3. 4,5-Dimethyl-6-aminopyrimidine. 4. 5-Ethyl-6-aminopyrimidine.

Neither in the oxy nor the amino series is the effect of the number and position of substituent alkyls upon absorption sufficiently well differentiated to justify a broad generalization, although a considerable degree of consistency can be observed.

Experimental

4-Methyl-6-oxypyrimidine.—Two hundred and sixty-five cc. of 12% hydrogen peroxide was warmed to 70° to start reaction and 20 g. of 4-methyl-2-thio uracil[2] was added with stirring in small portions to avoid rise of temperature above 90°. The solution was evaporated to small volume, made alkaline with sodium carbonate and brought to dryness on the steam-bath. The residue was extracted with benzene, the benzene evaporated and the residue sublimed in high vacuum at 100–110°. Sublimate was recrystallized from ethyl acetate, m. p. 148–149°; yield 8 g.

Anal. Calcd. for $C_5H_6N_2O$: C, 54.54; H, 5.45; N, 25.45. Found: C, 54.93, 54.98; H, 5.28, 5.39; N, 25.71.

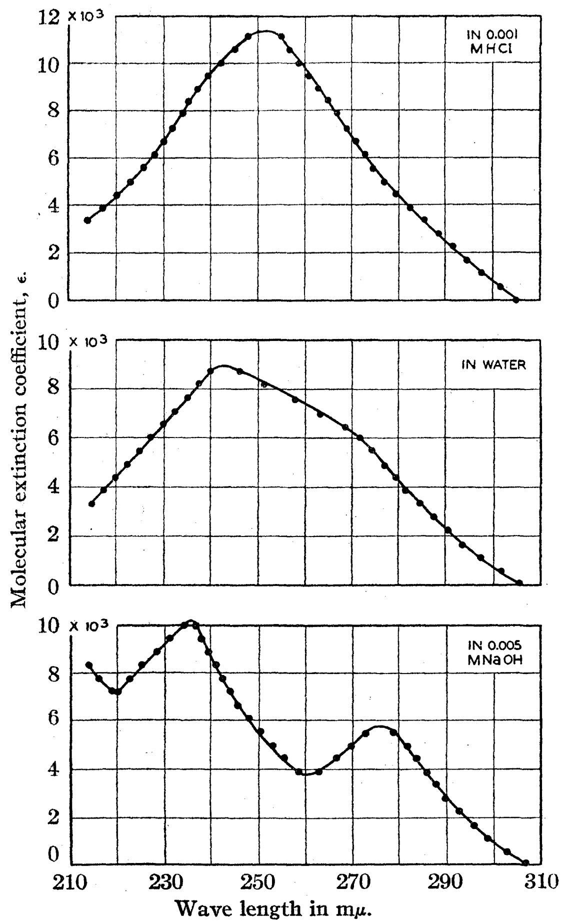

Fig. 6.—(a) In 0.001 M HCl, (b) in water, (c) in 0.005 M NaOH. Amino sulfonic acid.

This compound was prepared by Gabriel and Colman[5] from 4-methyl-2,6-dichloropyrimidine who found the m. p. 149–150°.

4-Methyl-6-aminopyrimidine.—One gram of 4-methyl-6-chloropyrimidine was heated with alcoholic ammonia at 110° for ten hours, the solution evaporated to dryness, the residue taken up in a minimum amount of water, potassium hydroxide added while cooling with ice and the crystalline product filtered off, recrystallized from hot water and sublimed in high vacuum at 85–90°; yield 0.4 g.; m. p. 194–195°.

Anal. Calcd. for $C_5H_7N_3$: N, 38.53. Found: N, 38.52, 38.52.

The same substance, prepared by Gabriel and Colman[5] from 2-chloro-4-methyl-6-aminopyrimidine, melted at 194–195°.

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[5] Gabriel and Colman, *Ber.*, **32**, 2929 (1899).

5-Methyl-6-oxypyrimidine.—Seven and one-half grams of thiothymine[6] was oxidized with hydrogen peroxide as described above for methyl thiouracil. The solution was made alkaline with ammonia and evaporated to dryness. The residue was extracted with chloroform, the chloroform solution dried and evaporated and the residue sublimed in high vacuum at 110°, yielding 4.14 g. of a compound melting at 153–154°.

Anal. Calcd. for $C_5H_6N_2O$: C, 54.54; H, 5.45; N, 25.45. Found: C, 54.90, 54.81; H, 5.10, 5.32; N, 25.05, 25.17.

5-Methyl-6-aminopyrimidine.—One gram of the above compound was warmed gently in a water-bath with 4 cc. of phosphorus oxychloride until completely in solution. The solution was evaporated *in vacuo* to one-half volume and added to crushed ice, made alkaline with sodium hydroxide and extracted with chloroform. The extract was dried and evaporated *in vacuo* at 20° leaving an oil which did not crystallize. This was heated at 120° for eight hours with excess alcoholic ammonia. The product was isolated as in the case of 4-methyl-6-aminopyrimidine and sublimed in high vacuum at 110°, yielding a white sublimate of m. p. 175–176°.

Anal. Calcd. for $C_5H_7N_3$: C, 55.05; H, 6.42; N, 38.53. Found: C, 55.48, 55.71; H, 6.47, 6.46; N, 38.88, 38.60.

This compound was prepared from 4-iodo-5-methyl-6-aminopyrimidine by Gerngross[7] who recorded its melting point as 176°.

2-Thio-4,5-dimethyl-6-oxypyrimidine.—Seventy-two grams of thiourea and 132 g. of ethyl α-methylacetoacetate were refluxed with stirring on a steam-bath with 21 g. of sodium dissolved in 500 cc. of absolute alcohol for three hours. The reaction mixture was evaporated on the steam-bath nearly to dryness, cooled and acidified with acetic acid. After standing in an ice-box overnight the crystalline precipitate was collected and recrystallized first from 95% alcohol and then from absolute. The substance does not melt up to 255°; yield 88 g.

Anal. Calcd. for $C_6H_8N_2OS$: C, 46.15; H, 5.13; N, 17.95. Found: C, 46.17; H, 5.20; N, 18.19.

4,5-Dimethyl-6-oxypyrimidine.—Ten grams of the above thiopyrimidine was oxidized with hydrogen peroxide and the product was isolated as in the case of 5-methyl-6-oxypyrimidine. Instead of subliming it was recrystallized from hot ethyl acetate in which it is sparingly soluble; m. p. 202–203°; yield 4.22 g.

Anal. Calcd. for $C_6H_8N_2O$: C, 58.06; H, 6.45; N, 22.58. Found: C, 58.23, 58.13; H, 6.42, 6.37.

Schlenker[8] prepared this substance, m. p. 204°, by reducing the 2,6-dichloro-4,5-dimethylpyrimidine.

4,5-Dimethyl-6-chloropyrimidine.—2.2 grams of the 6-oxy compound was converted to the 6-chloro derivative as in the case of the 5-methyl-6-oxy analog. The solid product was sublimed in high vacuum at 50°; m. p. 52°; yield 1.57 g.

Anal. Calcd. for $C_6H_7N_2Cl$: C, 50.53; H, 4.91; N, 19.65. Found: C, 50.93, 50.79; H, 4.93, 4.82; N, 19.55, 19.46.

Schlenker[8] has reported this compound melting at 51°.

4,5-Dimethyl-6-aminopyrimidine.—One gram of the above chloro derivative was converted to the corresponding amino by heating for fifteen hours at 110° with alcoholic ammonia. Isolation was effected as in the case of the previous aminopyrimidines; purification by recrystallization first from hot water and then from benzene; m. p. 229–231°; yield 0.35 g.

Anal. Calcd. for $C_6H_9N_3$: C, 58.54; H, 7.32; N, 34.15. Found: C, 58.32; H, 7.39; N, 34.37.

Schlenker[8] prepared this compound from 2-chloro-4,5-dimethyl-6-aminopyrimidine and recorded the m. p. as 230°.

2,5-Dimethyl-6-oxypyrimidine.—Forty-two grams of ethyl sodioformylpropionate[6] and 26 g. of acetamidine hydrochloride were dissolved in 200 cc. of water and allowed to stand for two days. The solution was evaporated on the steam-bath until crystallization started, made alkaline with ammonia and repeatedly extracted with chloroform. The extract was dried over sodium sulfate and evaporated to dryness *in vacuo.* The residue was sublimed in high vacuum at 125°, and the sublimate was recrystallized twice from acetone; m. p. 174°; yield, approximately 6 g.

Anal. Calcd. for $C_6H_8N_2O$: C, 58.06; H, 6.45; N, 22.58. Found: C, 58.22, 57.96; H, 6.36, 6.30; N, 23.23, 23.29.

2,5-Dimethyl-6-chloropyrimidine.—2.58 grams of 2,5-dimethyl-6-oxypyrimidine was converted to the chloro derivative in the usual way. The crude product was distilled at 40 mm. yielding a colorless oil which, due to its volatility, could not be weighed readily for satisfactory micro-analyses.

2,5-Dimethyl-6-aminopyrimidine.—One gram of the above 2,5-dimethyl-6-chloro pyrimidine was heated with excess alcoholic ammonia in a sealed tube at 125° for seven hours. Isolation of the product proceeded as in the case of other 6-aminopyrimidines. The product was purified by sublimation at 80°; m. p. 201–202°; yield 0.35 g.

Anal. Calcd. for $C_6H_9N_3$: C, 58.54; H, 7.31; N, 34.15. Found: C, 58.95, 59.02; H, 6.94, 7.20; N, 33.74, 33.63.

Picrate from water solution with aqueous picric acid, m. p. 222°.

Anal. Calcd. for $C_{12}H_{12}N_6O_7$: N, 23.87. Found: N, 24.10.

Approximate colorimetric determinations of the *p*H of water solutions of each of the aminopyrimidines were made using meta cresol purple and thymol blue as indicators. The solutions were approximately 0.01 *M* except in the case of 5-ethyl-6-amino which was insufficiently soluble and was, therefore, tested as a saturated solution.

TABLE I

ALKALINITY OF 6-AMINOPYRIMIDINE SOLUTIONS

Base	Solubility	*p*H
6-Amino	Moderate	8.3
2-Methyl-6-amino	Free	8.6–8.7
4-Methyl-6-amino	Moderate	8.3
5-Methyl-6-amino	Moderate	8.3
5-Ethyl-6-amino	Very sparing	7.9–8.0
2,4-Dimethyl-6-amino	Free	8.6–8.7
2,5-Dimethyl-6-amino	Sparing	8.5–8.6
4,5-Dimethyl-6-amino	Sparing	8.2–8.3

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(6) Wheeler and McFarland, *Am. Chem. J.*, **43**, 19 (1910).

(7) Gerngross, *Ber.*, **38**, 3403 (1905).

(8) Schlenker, *ibid.*, **34**, 2823 (1901).

The ultraviolet absorption of all of the compounds was measured with a Hilger "Spekker" Photometer in conjunction with a Hilger E316 spectrograph. The source was a tungsten steel spark in some cases and a wide aperture hydrogen discharge tube in others. Either source was satisfactory. The Spekker photometer gave much more satisfactory results than the rotating sector used for earlier work.[9] Eastman d. c. Ortho and Cramer Contrast plates were both used with success. Solutions were in distilled water unless otherwise indicated.

We wish to express our gratitude to Mr. D. F. Hayman and Mr. S. Adler for the micro-analyses, to Dr. Joseph K. Cline for the preparation of 2-methyl-6-oxy- and 2-methyl-6-aminopyrimidines, to Mr. R. E. Waterman for the *p*H determinations and to Dr. H. T. Clarke for the use of facilities in preparing some of the spectrograms.

Summary

1. Methods of preparation are given for all of the previously unknown mono- and di-C-methyl derivatives of 6-oxy and 6-aminopyrimidine.

2. The ultraviolet absorption is given of both complete series including the non-alkylated members.

3. Addition of acid modifies the absorption of the 6-amino pyrimidines by reducing the prominence of the longer wave length band; alkali tends to equalize the prominence of the two bands.

4. The absorption of aminosulfonic acid from the vitamin reveals the influence of the acidity of the sulfonic group and is affected by alkali in a similar manner as non-sulfonated 6-aminopyrimidines.

New York, N. Y.
Rahway, N. J. Received December 30, 1936

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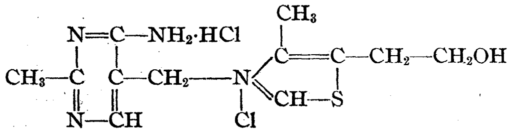
[9] Wintersteiner, Williams and Ruehle, This Journal, **57**, 517 (1935).

[Contribution from Research Laboratory, Merck and Company, and Private Laboratories]

Studies of Crystalline Vitamin B_1. XVI. Identification of the Pyrimidine Portion

By Joseph K. Cline, Robert R. Williams, A. E. Ruehle and Robert E. Waterman

In a recent communication[1] the structure



was assigned to vitamin B_1 (aneurin) upon the basis of evidence which was indicated briefly at that time. Since then this structure has been confirmed by our synthesis[2] of the vitamin, by Grewe's synthesis[3] of two cleavage products, $C_6H_{10}N_4$, obtained from the vitamin by Windaus and collaborators,[4] and the amino sulfonic acid described previously[5] by our own group of associates, and finally by Bergel and Todd's synthesis of thiochrome.[6] Except for some questions which have not yet been fully resolved about possible stereoisomerism of the vitamin, the structure of the substance is established. The purpose of this paper is therefore merely to relate in greater detail the experimental evidence upon which our conclusions were based.

The earliest clear evidence of a bridge between the two nuclei in the vitamin came to us through the discovery that the vitamin is split at room temperature in liquid ammonia solution yielding a base, $C_6H_{10}N_4$, whose picrate melts at 225° and is evidently identical with the picrate of Windaus.[4] The base exhibits absorption in the ultraviolet characteristic of a C-alkylated 6-aminopyrimidine rather than a diaminopyrimidine. In Fig. 1 the absorption curve of this base is compared with those of 2,5-dimethyl-6-aminopyrimidine,[7] 4-methyl-5,6-diaminopyrimidine,[8] 4,5-dimethyl-2,6-diaminopyrimidine[9] and 5-ethyl-4,6-diaminopyrimidine.[10] These curves for diaminopyrimidines representing the several possible positions on the ring of the second amino group all differ radically from that for the base obtained from the vitamin. The latter substance, however, resembles in absorption the mono- and dialkylated 6-aminopyrimidines as displayed in the preceding paper[7] as well as the sodium salt of the amino sulfonic acid and the free oxysulfonic acid previously de-

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[1] This Journal, **58**, 1063 (1936).

[2] *Ibid.*, **58**, 1504 (1936).

[3] R. Grewe, *Z. physiol. Chem.*, **242**, 89 (1936).

[4] A. Windaus, T. Tschesche and R. Grewe, *ibid.*, **237**, 98 (1935).

[5] This Journal, **57**, 1093 (1935).

[6] Bergel and Todd, *Nature*, **138**, 406 (1936).

[7] Williams, Ruehle and Finkelstein, This Journal, **59**, 526 (1937).

[8] Gabriel and Colman, *Ber.*, **34**, 1245 (1901).

[9] Schlenker, *ibid.*, **34**, 2826 (1901).

[10] A. v. Merkatz, *ibid.*, **52**, 874 (1919).

rived from the vitamin. The resemblance to 2,5-dimethyl-6-aminopyrimidine is particularly close. Bearing in mind the influence of alkali upon the absorption of 6-aminopyrimidines and upon that of the aminosulfonic acid, the added basicity of the second amino group in the base $C_6H_{10}N_4$ would be expected to operate in the same direction. Since the absorption of the diamino base closely resembles those of the monoaminopyrimidines when the latter are observed in alkaline solution, we concluded that the second amino group is in a side chain. This side chain is common also to the aminosulfonic acid and therefore to the vitamin itself. This conclusion was fortified by the observation that groups other than amino in side chains influence the absorption only to a minor degree. Thus as we shall show in a later paper, ethoxymethyl, bromomethyl, carbethoxymethyl, or sulfomethyl groups on the pyrimidine ring behave in general somewhat as unsubstituted methyl groups in their influence on ultraviolet absorption of 6-amino and 6-oxy derivatives.

While the attachment of the second amino group to a side chain was clear, one could not be certain of the position of the side chain from absorption evidence alone. Now that the position of this side chain has been fixed by other independent evidence, the better correlation in absorption of the base $C_6H_{10}N_4$ with 2,5-dimethyl-6-amino-pyrimidine than with the other dimethylated 6-amino compounds is seen to be significant.

Satisfactory comparison of absorption curves cannot be made in the form of the picrates on account of the strong absorption of picric acid. Hydrochlorides are also unsatisfactory, as these on account of their acidity display only single banded and therefore less distinctive absorption.

In the light of this evidence, the aminosulfonic acid was reduced with metallic sodium in liquid ammonia solution. The larger part of the pyrimidine appeared as unidentifiable amorphous, insoluble and unsublimable products, possibly resulting from coupling of two rings.[11] We were, however, able to isolate a small yield of a base, m. p. 202°, which formed a picrate, m. p. 221–222°, identical by mixed melting point with that of 2,5-dimethyl-6-aminopyrimidine.[7] This provided the first unequivocal evidence of the positions of alkylation as well as final confirmation of the presence of the 6-aminopyrimidine nucleus in the vitamin.

Accepting the above evidence for 2,5-methylation, it was still necessary to determine whether the thiazole of the vitamin was located on the 2- or the 5-side chain. Consideration of the evidence as to the structure of thiochrome[4,12] led us to prefer the 5-position, our process of reasoning following the general lines upon which Makino and Imai[13] based their suggestion of the possibility of a methylene bridge. We had prepared synthetically, as will appear in a later paper, several 6-oxypyrimidines[1] with an ethoxymethyl group in various other positions. By treating 2-methyl-6-oxy-5-ethoxymethylpyrimidine with sodium sulfite, we were able to reproduce the oxy-sulfonic acid[5] previously derived from the vitamin and thus fixed the final detail of the structure of the latter.

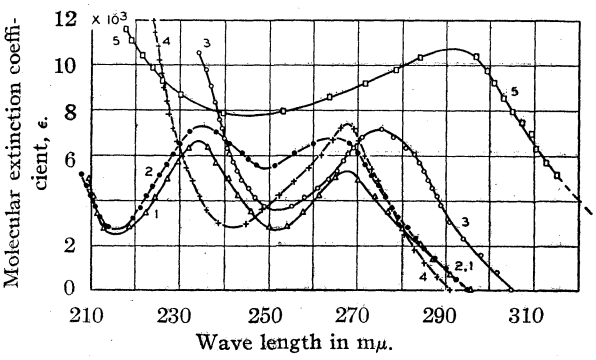

Fig. 1.—

1. Liquid ammonia cleavage product of vitamin.
2. 2,5-Dimethyl-6-aminopyrimidine.
3. 4,5-Dimethyl-2,6-diaminopyrimidine.
4. 5-Ethyl-4,6-diaminopyrimidine.
5. 4-Methyl-5,6-diaminopyrimidine.

Experimental Part

Liquid Ammonia Cleavage of Vitamin.—212 mg. of vitamin hydrochloride was dried for two hours at 80° *in vacuo* in a fragile glass bulb which was sealed off at the end of the drying period and transferred to a heavy-walled bomb tube. The latter was then connected to a system consisting of liquid ammonia cylinder, soda lime tube and a bomb tube with side-arm containing metallic sodium. The glass system was then evacuated and dried, liquid ammonia was admitted and condensed upon the sodium by packing the appropriate tube in solid carbon dioxide. Thence the ammonia was distilled off into the bomb tube containing the vitamin within the small tube. This bomb tube was sealed off and the bulb within was broken by shaking. The vitamin dissolved with a light brown color

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(11) Kircher, *Ann.*, **385**, 295 (1911).

(12) Barger, Bergel and Todd, *Ber.*, **68**, 2257 (1935); Kinnersley O'Brien and Peters, *Biochem. J.*, **29**, 2369 (1935).

(13) K. Makino and T. Imai, *Z. physiol. Chem.*, **239**,1 (1936).

which, as the ammonia approached room temperature, turned to a deep green which grew in intensity for a half hour then slowly faded over a period of forty-two hours at room temperature. The tube was then cooled and opened and the ammonia distilled off under anhydrous conditions and finally *in vacuo*. A light colored gummy mass containing much crystalline matter remained. This was extracted successively with 8-, 5- and 3-cc. portions of chloroform. On evaporation of the chloroform, 129.8 mg. of oil remained which on analysis contained 3% sulfur.

This oil after standing for a week was no longer fully soluble in chloroform. On extracting successively with 3-, 2- and 2-cc. portions of chloroform, the combined extracts left a partly crystalline residue of 88.3 mg. This was treated with 4 drops of water and the insoluble residue washed successively with 2, 2 and 1 drops of water. The aqueous solution was evaporated to dryness leaving a yellow crystalline mass which was washed with 0.5 cc. of an equal volume mixture of chloroform–alcohol and finally recrystallized three times from hot absolute alcohol; yield 13.9 mg. of dense colorless columnar crystals growing in rosets; m. p. 211–215°. The ultraviolet absorption in water solution is shown in Fig. 1.

Anal. Calcd. for $C_6H_{10}N_4$: C, 52.17; H, 7.25; N, 40.58. Found: C, 51.35; H, 6.35; N, 38.53.[14]

Dumas nitrogen determinations in these pyrimidines are troublesome.[15] The method here used was one devised by Hayman[16] and previously tested on a series of synthetic pyrimidines of similar structure.

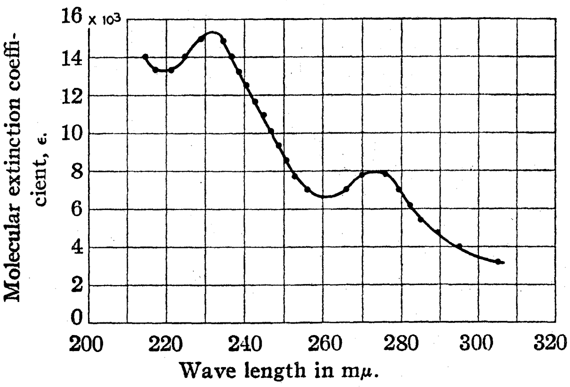

Fig. 2.—4-Methyl-5-formylamino-6-aminopyrimidine.

A portion of the base was converted to the hydrochloride and treated in aqueous solution with picric acid to incipient precipitation. On standing overnight rosets of yellow needles appeared; m. p. 225°.

Anal. Calcd. for $C_6H_{10}N_4[C_6H_2OH(NO_2)_3]_2$: C, 36.24; H, 2.68; N, 23.49. Found: C, 36.94; H, 2.56; N, 23.80.

The fate of the thiazole portion of the molecule was not determined. Considerable evolution of hydrogen sulfide was noted on distilling one of the by-products *in vacuo* and it seems probable that an extensive degradation occurs. The thiazole by itself does not give the green color in liquid ammonia.

Preparation of Diaminopyrimidines.—The preparation of 4-methyl-5,6-diaminopyrimidine,[8] 4,5-dimethyl-2,6-diaminopyrimidine[9] and 5-ethyl-4,6-diaminopyrimidine[10] followed the literature. It should be added that in preparing the last named from 4-iodo-5-ethyl-6-aminopyrimidine it was necessary to heat with saturated alcoholic ammonia at 220° for fifteen hours. The product melted at 235–237° compared with the literature figure of 233–235° but on further purification by sublimation or recrystallization from ethyl acetate, melted at 245°. It formed a dipicrate, m. p. 165–167°.

Anal. Calcd. for $C_6H_{10}N_4[C_6H_2OH(NO_2)_3]_2$: N, 23.49. Found: N, 23.68.

4-Ethyl-5,6-diaminopyrimidine[17] was also prepared by Dr. E. R. Buchman in a manner analogous to that of the cited literature[8] for 4-methyl-5,6-diamino. Dr. Buchman kindly supplied a sample for ultraviolet examination. Its absorption is almost identical with that of the 4-methyl analog. The formyl derivatives of the 5,6-diamino compounds show a striking modification of absorption (see Fig. 2).

Reduction of Amino Sulfonic Acid with Sodium.—27 mg. of the aminosulfonic acid was suspended in 5 cc. of anhydrous liquid ammonia (distilled from sodium) and 10 mg. of metallic sodium was added in portions with shaking. After standing a half hour, the ammonia was evaporated by passing in a stream of dry air. A few drops of alcohol were added to destroy any excess of sodium and the residue sublimed *in vacuo* at about 120° at 0.1 mm., and then at atmospheric pressure at 180–200°. The final sublimate melted sharply at 202°.

Anal. Calcd. for $C_6H_9N_3$: C, 58.54; H, 7.32; N, 34.15. Found: C, 58.34; H, 7.40; N, 33.67.

An aqueous solution of the sublimate was treated with aqueous picric acid solution to faint opalescence. Upon standing overnight needle crystals of a picrate separated which melted at 221–222°. When mixed with the picrate of 2,5-dimethyl-6-aminopyrimidine, the melting point was not depressed.

Anal. Calcd. for $C_6H_9N_3C_6H_2OH(NO_2)_3$: N, 23.86. Found: N, 23.41.

Synthesis of Oxysulfonic Acid.—300 mg. of 2-methyl-5-ethoxymethyl-6-oxypyrimidine prepared according to a method to be described in a later paper was dissolved in 5 cc. of water containing 1 g. of sodium sulfite. The mixture was saturated with sulfur dioxide and heated for eighteen hours at 144° in a sealed tube. To the pale yellow solution concentrated hydrochloric acid was added and the solution was saturated with dry hydrogen chloride to precipitate sodium chloride. The filtrate from the sodium chloride was concentrated to a small volume, again saturated with hydrochloric acid to remove further sodium chloride. After removing sodium chloride as completely as possible, the oily residue was dissolved in 3 cc. of water and 8 cc. of alcohol was added. On standing white crystals separated. These were purified by dissolving in 3 cc. of concentrated hydrochloric acid, centrifuging off a trace

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(14) This analysis was made after heating *in vacuo* to 100° for one hour during which a small loss of weight occurred. Previous to this heating values for C and H of 50.66 and 5.98%, respectively, were obtained. The results suggested that the base absorbs carbon dioxide from the air.

(15) Milner and Sherman, *Ind. Eng. Chem., Anal. Ed.*, **8**, 331 (1936).

(16) D. F. Hayman and S. Adler, *ibid.*, in press.

(17) Robinson and Tomlinson, *J. Chem. Soc.*, II, 1283 (1935).

of insoluble matter, evaporating to dryness and recrystallizing from water and alcohol as before. The crystals did not melt up to 360°.

Anal. Calcd. for $C_6H_8N_2SO_4$: C, 35.27; H, 3.95; N, 13.73; S, 15.69. Found: C, 35.23, 35.53; H, 3.78, 3.89; N, 14.06, 13.78; S, 15.30, 15.33.

Through the kindness of Mr. H. W. Hermance the crystals were compared crystallographically with the natural oxysulfonic acid obtained from the vitamin. He reported: "The bulk of the crystals of the synthetic sulfonic acid occurred in the form of slightly tapering rods, 50–100 microns in length, with a sharp terminal angle (not measured because of the smallness of the crystal). Some twinning was observed but individually developed crystals were more general. The extinction angle, measured from the long edge, was fairly constant through about twenty observations. It was found to be 59 ± 0.5°. The crystals appeared to belong either to the monoclinic or triclinic system. As oriented on the slide, two indices of refraction were evident. The higher, observed at the extinction position, was slightly greater than 1.632, the lower, slightly less than 1.623.

"The natural oxysulfonic acid corresponded in the above crystallographic constants with the synthetic within the limits of experimental error. It showed a somewhat greater tendency to twinning which, however, cannot be regarded as evidence of a difference in molecular structure."

The synthetic sulfonic acid was also compared with the natural with respect to ultraviolet absorption. Close agreement was observed (Fig. 3). Since no melting point was available as a criterion of identity, and since experience with alkylated oxypyrimidines[7] had indicated that ultraviolet absorption is not a definitive index of the position of alkyl substituents, it still appeared possible that the synthetic oxysulfonic acid was merely isomeric and not identical with the natural. This was especially true since all such sulfonic acids might be expected also to resemble one another in other physical properties, such as solubilities. Under these circumstances resort was had to a special form of solubility comparison. Portions of absolute ethyl alcohol were saturated with (a) the natural sulfonic acid, (b) the synthetic and (c) both synthetic and natural. The intensities of ultraviolet absorption of these three solutions were then compared and found to be identical throughout the range of frequency. If the substances were not identical, solution (c) should have absorbed with an intensity approximating that of (a) + (b). In making such comparisons, it was found essential to clarify the solutions thoroughly. This was done by centrifuging in a horizontal position in the optical cells in which solution had been effected so that any sediment deposited on the cylindrical walls. It was of course necessary to check carefully the equality of intensity of illumination produced by the two parallel beams of light.

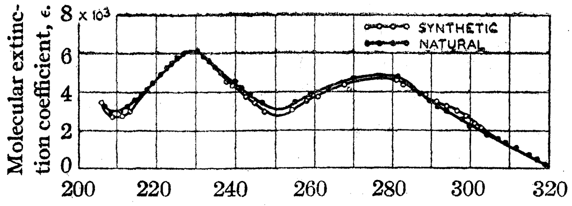

Fig. 3.—2-Methyl-6-oxy-5-methylsulfonic acid.

We gratefully acknowledge our indebtedness to Mr. D. F. Hayman and Mr. S. Adler for the microanalyses, to Mr. J. Finkelstein for the synthesis of 2,5-dimethyl-6-amino- and several diaminopyrimidines, as well as to Dr. E. R. Buchman and Mr. H. W. Hermance for the courtesies noted in the text. Thanks are also due to Dr. R. T. Major for advice and for facilities put at our disposal.

Summary

1. The vitamin undergoes cleavage with liquid ammonia producing a base, $C_6H_{10}N_4$, which exhibits ultraviolet absorption akin to that of C-methylated-6-aminopyrimidines but unlike that of 6-aminopyrimidines having another amino group elsewhere on the ring.

2. Reduction by means of sodium in liquid ammonia of the aminosulfonic acid obtained by sulfite cleavage of the vitamin yields 2,5-dimethyl-6-aminopyrimidine.

3. Reaction of sulfite with 2-methyl-5-ethoxymethyl-6-oxypyrimidine yields 2-methyl-6-oxypyrimidine-5-methylsulfonic acid which is identical with the oxy-sulfonic acid previously derived from the vitamin.

4. The structure of the vitamin is thereby established.

NEW YORK, N. Y.
RAHWAY, N. Y.

RECEIVED DECEMBER 30, 1936

[Contribution from the College of Pharmacy, University of Michigan]

Arsinic Acids[1]

By F. F. Blicke and G. L. Webster[2]

The object of this paper is to describe the preparation and properties of a number of arsinic acids and their derivatives which were prepared in connection with our study of diarsyls.

By means of an unusual process, namely, treatment of diazotized 2-aminophenylarsonic acid with sulfur dioxide, Kalb[3] obtained a substance which he claimed to be an anhydride of the dihydroxy form of 2-hydroxyphenylarsine oxide, $C_6H_4(OH)As(OH)_2$, but the only experimental evidence offered in support of his structure was an arsenic analysis.

We prepared Kalb's product by means of a more orthodox procedure, that is, hydrolysis of 2-hydroxyphenyldichloroarsine. Both an arsenic analysis and a molecular weight determination offer strong support for the anhydride formula and it seems that this oxide does not exist in the ordinary form $C_6H_4(OH)As{=}O$.

Experimental Part

2- and 3-Aminodiphenylarsinic Acid.—Reduction of 25 g. of the required nitro acid, dissolved in 20 g. of sodium hydroxide and 250 cc. of water, was effected with ferrous hydroxide obtained by addition of 61 g. of sodium hydroxide in 235 cc. of water to 195 g. of ferrous sulfate dissolved in 400 cc. of water. After twenty-four hours the mixture was filtered and the filtrate carefully acidified; yield 15 g. of the 2-amino acid and 16 g. of the 3-amino compound.

2-Hydroxydiphenylarsinic Acid.—A solution, prepared from 27.7 g. of 2-aminodiphenylarsinic acid, 160 cc. of water and 20 cc. of concd. sulfuric acid, was poured onto 400 g. of ice and diazotized with 15.2 g. of sodium nitrite, whereupon a slow evolution of nitrogen began almost immediately. After twenty-four hours the dark brown precipitate of hydroxy acid was filtered; yield 25 g. or 90% of the calcd. amount.

2-Methoxydiphenylarsinic Acid.—A mixture, composed of 5.5 g. of 2-hydroxydiphenylarsinic acid, 20 cc. of water, 5.0 g. of sodium hydroxide and 3.6 cc. of dimethyl sulfate, was shaken until the sulfate had disappeared; the methylation process was repeated four times. The mixture was heated on a steam-bath for one-half hour, partially neutralized with 20 cc. of hydrochloric acid, treated with charcoal and filtered. The cold filtrate was acidified to congo red; yield 5.2 g.

3-Nitrodiphenylarsinic Acid.—A solution, prepared from 27.6 g. of technical 3-nitroaniline, 50 cc. of hydrochloric acid and 100 cc. of water, was diazotized with 13.8 g. of sodium nitrite, dissolved in 400 cc. of water, the mixture then diluted with 1000 cc. of water and treated with 5 *N* sodium hydroxide until no longer acid toward congo red.

To the stirred diazonium solution, maintained at 15°, there was added, slowly, 33.6 g. of phenylarsine oxide, dissolved in a mixture of 40 cc. of 10 *N* sodium hydroxide and 180 cc. of water. The mixture was stirred for two hours, made slightly acid with acetic acid, filtered and the filtrate acidified with hydrochloric acid until acid to congo red; the precipitated arsinic acid weighed 16.5 g. The filtrate was neutralized with sodium hydroxide and evaporated to a volume of 300 cc., cooled, made slightly acid with acetic acid, filtered and the filtrate acidified to congo red; 16 g. more of the arsinic acid precipitated; total yield 51% of the calcd. amount.

4-Bromodiphenylarsinic Acid.—A solution of 172 g. of 4-bromoaniline in 350 cc. of hydrochloric acid and 400 cc. of water was poured onto 1000 g. of ice, 1000 cc. of water added and more ice, if necessary to keep the temperature at 0°. The amine was diazotized with 70 g. of sodium nitrite, dissolved in 500 cc. of water.

A solution, prepared from 170 g. of phenylarsine oxide, 160 g. of flake sodium hydroxide and 3000 cc. of water, was added to the diazonium solution during the course of one hour and the mixture was stirred vigorously for three hours. After twelve hours it was filtered. The tarry residue contained 4-chlorobromobenzene. The filtrate was shaken with charcoal, filtered and acidified to congo red with hydrochloric acid; yield 137 g.

3,4′-Dinitrodiphenylarsinic Acid.—The solution, obtained by sifting 30.7 g. of 4-nitrodiphenylarsinic acid[4] onto 100 cc. of concd. sulfuric acid, was cooled to 0°, stirred, and treated, dropwise, with a mixture of 6.4 cc. of nitric acid (sp. gr. 1.42) and 6.4 cc. of sulfuric acid while the temperature was maintained at 0–3°. After twelve hours the mixture was poured onto 700 g. of ice, the yellow, crystalline nitro acid filtered and washed with water; yield 35.0 g.; calcd. yield 35.2 g.

3,4′-Dihydroxydiphenylarsinic Acid.—A solution, prepared from 3.6 g. of 3,4′-diaminodiphenylarsinic acid, 5 cc. of sulfuric acid and 50 cc. of water, was diazotized at 0–5° with 2.0 g. of sodium nitrite dissolved in 10 cc. of water. The mixture was heated for two hours at 55–65°, the liquid decanted from a small amount of red by-product, cooled with ice and stirred. The red gum which separated was discarded. After some time the dihydroxy acid separated from the clear solution in a colorless, crystalline form.

3,3′-Dinitro-4-hydroxydiphenylarsinic Acid.—Twenty-one grams of 4-hydroxydiphenylarsinic acid,[4,5] dissolved in

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[1] This paper represents part of a dissertation submitted to the Horace H. Rackham School of Graduate Studies by G. L. Webster in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] University Fellow in the Horace H. Rackham School of Graduate Studies.

[3] Kalb, *Ann.*, **423**, 52, 70 (1921).

[4] Blicke and Oneto, This Journal, **56**, 685 (1934).

[5] If the solution of diazotized 4-aminophenylarsonic acid is heated to 65–70° for one hour, instead of at the boiling point, the yield of 4-hydroxydiphenylarsinic acid is increased to 75% of the calcd. amount.

TABLE I

ARSINIC ACIDS

Compounds 3, 10, 13 and 14 were recrystallized from water, 1, 4 and 11 from 15% acetic acid, 2 and 9 from 40% acetic acid, 5 from 20% alcohol, 6 and 7 from 50% alcohol and 8 and 12 from 85% alcohol. All of the acids are soluble in acetic acid and insoluble in benzene.

		M. p., °C.	Formula	As, % Calcd.	As, % Found
1	2-Aminodiphenyl	129–130[a]	....	...	...
2	2-Hydroxydiphenyl	221–223	$C_{12}H_{11}O_3As$	26.95	26.85
3	2-Methoxydiphenyl	187–188	$C_{13}H_{13}O_3As$	25.65	25.69
4	3-Nitrodiphenyl	154–155	$C_{12}H_{10}O_4NAs$	24.41	24.33
5	3-Aminodiphenyl	210–212	$C_{12}H_{12}O_2NAs$	27.05	27.13
6	3-Hydroxydiphenyl[b]	230–232	$C_{12}H_{11}O_3As$	26.95	26.99
7	3-Methoxydiphenyl[c]	120–121	$C_{13}H_{13}O_3As$	25.65	25.44
8	4-Bromodiphenyl	184–185	$C_{12}H_{10}O_2BrAs$	(23.44	23.60 % Br)
9	3,4′-Dinitrodiphenyl	230–232	$C_{12}H_9O_6N_2As$	21.28	21.41
10	3,4′-Diaminodiphenyl[d]	176–178	$C_{12}H_{13}O_2N_2As$	25.65	25.77
11	3,4′-Dihydroxydiphenyl	210–211	$C_{12}H_{11}O_4As$	25.48	25.76
12	3,3′-Dinitro-4-hydroxydiphenyl	195–196	$C_{12}H_9O_7N_2As$	20.36	20.13
13	Methyl-3-amino-4-hydroxyphenyl[e]	233–234	....	...	...
14	Methyl-3-nitro-4-methoxyphenyl	216–217	$C_8H_{10}O_5NAs$	27.24	27.29

[a] Kalb [*Ann.*, **423**, 60 (1921)] reported the same melting point. [b] For preparative method see corresponding 2-hydroxy compound. [c] For preparative method see corresponding 2-methoxy compound. [d] For preparative method see corresponding 3,3′-diamino compound [Blicke, Oakdale and Oneto, THIS JOURNAL, **56**, 142 (1934)]. [e] Bertheim [*Ber.*, **48**, 358 (1915)] reported 206–207°.

105 cc. of concd. sulfuric acid, was nitrated very slowly with 9.6 cc. of nitric acid (sp. gr. 1.42) and an equal volume of concd. sulfuric acid while the temperature was maintained below 0°. After eight hours the mixture was poured onto 1000 g. of ice and the precipitated acid washed with water; yield 26.5 g. or 95% of the calcd. amount.

Methyl-3-amino-4-hydroxyphenylarsinic Acid.—To 185 g. of technical ferrous sulfate, dissolved in 650 cc. of water, and 200 g. of flake sodium hydroxide, dissolved in 300 cc. of water, there was added 26.1 g. of methyl-3-nitro-4-hydroxyphenylarsinic acid[6] dissolved in a mixture of 100 cc. of water and 10 g. of sodium hydroxide. The mixture was shaken vigorously in a stoppered flask for thirty minutes. After twenty-four hours the material was filtered and the filtrate made acid to congo red by the addition of approximately 280 cc. of concd. hydrochloric acid. The solution was then evaporated to a volume of about 600 cc., filtered, cooled and neutralized to congo red by the addition of sodium hydroxide solution. The amino acid precipitated when the sides of the container were scratched. The product was filtered and a further amount of acid obtained by concentration of the filtrate; yield 16.5 g. or 71% of the calcd. amount.

Methyl-3-nitro-4-methoxyphenylarsinic Acid.—A mixture of 12.2 g. of 3-nitro-4-methoxyphenylarsine oxide, 80 cc. of methyl alcohol, 6 g. of sodium hydroxide (70%) and 45 cc. of water was cooled and shaken with 4 cc. of methyl iodide in a stoppered flask. After twenty-four hours the mixture was filtered and then heated in an evaporating dish until a crust began to form on the surface of the liquid. The material was cooled, diluted with 25 cc. of water and 17 cc. of acetic acid added. The precipitated, crystalline arsinic acid weighed 13.5 g. which is 97% of the calcd. amount; m. p. 216–217° after recrystallization from water.

4-Bromophenylarsonic Acid.[7]—A solution of 172 g. of 4-bromoaniline, 300 cc. of hydrochloric acid and 400 cc. of water was poured onto 800 g. of ice, the mixture stirred and diazotized at 0° with 70 g. of sodium nitrite dissolved in 200 cc. of water. During this process the temperature should remain below 5°.

A mixture of 5 g. of copper sulfate, 50 cc. of water and 10 cc. of ammonia water was added to a solution of 210 g. of sodium arsenite and 250 g. of sodium carbonate in 2000 cc. of water. The mixture was cooled to 15°, stirred vigorously and the solution of the diazotized amine added slowly during the course of one hour. The material was stirred for two hours and after twelve hours was filtered; the filtrate was acidified to congo red with hydrochloric acid; yield 193 g.

4-Nitrophenyldichloroarsine.—One drop of hydriodic acid was added to 10 g. of 4-nitrophenylarsonic acid,[8] dissolved in 25 cc. of hydrochloric acid, the mixture treated with sulfur dioxide and the oily precipitate obtained extracted with benzene. Since the dichloroarsine would not solidify, a crystalline derivative was obtained in the following manner. One-half of the original benzene solution of the dichloroarsine was dried with calcium chloride and treated with the piperidine salt of N-pentamethylene dithiocarbamate.[9] After twenty-four hours the solvent was allowed to evaporate, the crystalline residue washed thoroughly with water and the dried material (8.9 g.) recrystallized from ethyl acetate; m. p. 177–178°. This product was 4-nitrophenylarsylene-N-pentamethylenedithiocarbamate, $(NO_2)C_6H_4As[S—C(S)—NC_5H_{10}]_2$.

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[6] Bertheim, *Ber.*, **48**, 357 (1915).

[7] An inadequately described procedure is found in the German patent 250,264. Mouneyrat (English patent 142,947) prepared the acid by a modified Bart reaction.

[8] Johnson and Adams, THIS JOURNAL, **45**, 1311 (1923).

[9] Blicke and Oakdale, *ibid.*, **54**, 2993 (1932).

TABLE II

ARSINES

	M. p., °C.	Formula	As, % Calcd.	As, % Found	Halide, % Calcd.	Halide, % Found
2-Nitrodiphenyliodo	113–114	$C_{12}H_9O_2NIAs$	18.68	18.77	I 31.66	31.51
2-Aminodiphenylchloro hydrochloride	.....	$C_{12}H_{12}NCl_2As$	...	...	Cl 22.41	22.41
2-Acetylaminodiphenyliodo[a]	147–148	$C_{14}H_{12}ONIAs$	18.14	18.44	I 30.74	30.74
2-Methoxydiphenyliodo[b]	68– 69	$C_{13}H_{12}OIAs$	19.41	19.56	I 32.89	32.84
3-Aminodiphenylchloro hydrochloride[c]	173–175	$C_{12}H_{12}NCl_2As$	23.71	23.79	Cl 22.41	22.51
3-Acetylaminodiphenyliodo[d]	146–147	$C_{14}H_{13}ONIAs$	18.14	17.92	I 30.74	30.86
4-Methoxyphenyldichloro[e]	49– 50[f]	....	...	...	...	...
Methyl-3-amino-4-hydroxyphenylchloro hydrochloride	178–180	$C_7H_{10}ONCl_2As$	27.76	27.63	...	...
Methyl-3-amino-4-hydroxyphenyliodo hydrochloride	136–137	$C_7H_{10}ONI_2As$	16.54	16.74	I 56.06	56.02

[a] Obtained when 5 g. of 2,2″-diacetyldiaminotetraphenylarsyl oxide was warmed with 20 cc. of hydriodic acid for a few minutes. [b] Prepared from 2 g. of 2-methoxydiphenylarsinic acid and 10 cc. of hydriodic acid. [c] Prepared in the same manner as the corresponding 2-amino compound. [d] The compound obtained by acetylation of 3.6 g. of 3,3″-diaminotetraphenylarsyl oxide was rubbed under 35 cc. of hydriodic acid, the acid decanted and 5 cc. of acetic acid added, whereupon the oily iodide became crystalline. [e] Prepared by shaking 5 g. of 4-methoxyphenylarsine oxide with 25 cc. of hydrochloric acid. [f] Michaelis and Weitz [*Ber.*, **20**, 51 (1887)] reported 48°.

Anal. Calcd. for $C_{18}H_{24}O_2N_3S_4As$: As, 14.49; S, 24.79. Found: As, 14.83; S, 24.72.

2-Nitrodiphenyliodoarsine.—Five grams of 2-nitrodiphenylarsinic acid was heated with 20 cc. of hydrochloric acid until the arsinic acid dissolved. A crystalline material, undoubtedly an addition product of the two acids, often begins to precipitate at this stage. After the addition of 5 cc. of water and several drops of hydriodic acid the mixture was saturated with sulfur dioxide. The chloroarsine, which precipitated as a gum, was washed with water. The gum was covered with ether, treated with ammonia water and the arsyl oxide produced dissolved in the ether. The ether solution was separated and the solvent allowed to evaporate. The yellow, crystalline residue (3.6 g.) of the arsyl oxide was pulverized and triturated with excess hydriodic acid. After some time the iodoarsine was filtered on a Jena filter.

2-Aminodiphenylchloroarsine Hydrochloride and 2,2″-Diaminotetraphenylarsyl Oxide.—A mixture of 2 g. of 2-aminodiphenylarsinic acid, 75 cc. of hydrochloric acid and two drops of hydriodic acid was saturated with sulfur dioxide, the precipitated chloroarsine hydrochloride filtered, dissolved in the least possible amount of water and precipitated by the addition of fuming hydrochloric acid.

To obtain the oxide the chloroarsine hydrochloride was dissolved in water, the solution shaken with charcoal, filtered and the filtrate treated with ammonia water, drop by drop, until no more oxide precipitated. The latter was extracted with ether, the solution dried and the solvent removed. The oxide was obtained as a semi-solid mass.

A mixture of 10 g. of the semi-crystalline 2,2″-diaminotetraphenylarsyl oxide and 25 cc. of acetic anhydride was heated until all of the oxide dissolved. White, glistening crystals separated when the mixture was cooled. The product is soluble in alcohol, hot acetone, benzene and acetic acid; m. p. 180–181° after recrystallization from acetic acid.

According to the analyses the acetylated oxide contains acetic acid of crystallization. The three analyses recorded below were made with material prepared at different times.

Anal. Calcd. for $C_{28}H_{26}ON_2As_2 + 1.5CH_3COOH$: As, 22.10. Found: As, 21.97, 22.09, 22.00.

Methyl-3-amino-4-hydroxyphenylchloroarsine Hydrochloride.—A mixture of 5 g. of methyl-3-amino-4-hydroxyphenylarsinic acid, 25 cc. of hydrochloric acid, 15 cc. of water and a drop of hydriodic acid was saturated with sulfur dioxide, the crystalline precipitate dissolved in 25 cc. of warm water, shaken with charcoal, filtered and the chloride hydrochloride precipitated with 25 cc. of hydrochloric acid.

Methyl-3-amino-4-hydroxyphenyliodoarsine Hydriodide.—A solution of 2.6 g. of methyl-3-amino-4-hydroxyphenylchloroarsine hydrochloride in 10 cc. of water was treated with 1.7 g. of sodium bicarbonate, dissolved in 15 cc. of water. The gummy precipitate was triturated with 10 cc. of hydriodic acid (sp. gr. 1.7), the crystalline iodide hydriodide dissolved in 5 cc. of water and precipitated by the addition of 10 cc. of hydriodic acid.

Anhydride of 2-Hydroxyphenylarsine Oxide.—The solution of 2-hydroxyphenylarsonic acid, obtained by coupling 9.3 g. of diazotized 2-aminophenol with sodium arsenite,[10] was made neutral to litmus with hydrochloric acid, filtered, boiled with charcoal, filtered again and acidified to congo red with hydrochloric acid. After several extractions with ether to remove phenol, 1 cc. of hydriodic acid was added and the solution treated with sulfur dioxide. The precipitated, oily dichloroarsine was stirred with 10 g. of sodium carbonate dissolved in water. The thick gum which formed became crystalline when the mixture was heated. After recrystallization from acetone the compound melted at 181–182°.[11]

Anal. Calcd. for $C_6H_4(OH)As{=}O$: As, 40.73; mol. wt., 184. Calcd. for anhydride, $C_{12}H_8O_3As_2$: As, 42.83; mol. wt., 350. Found: As, 42.86; mol. wt., 341.[12]

3-Nitro-4-methoxyphenylarsine Oxide.—Twenty grams of 3-nitro-4-methoxyphenylarsonic acid[13] was dissolved in 1800 cc. of hot water, the solution cooled to 55° and a mixture of 10 cc. of sulfuric acid and 50 cc. of water added. After the addition of 4 cc. of hydriodic acid, sulfur dioxide was led into the hot solution for two hours. After

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(10) Bart, *Ann.*, **429**, 90 (1922).

(11) Kalb [*ibid.*, **423**, 70 (1921)] reported 177°.

(12) Determined by Menzies' method in acetone.

(13) Fargher, *J. Chem. Soc.*, **117**, 865 (1920).

twelve hours the precipitated oxide was filtered; yield 16.5 g. or 94% of the calcd. amount.

The oxide is insoluble in all of the common organic solvents but dissolves in sodium hydroxide solution and precipitates upon the addition of acid. For analysis the crude oxide was washed with hot 10% sodium carbonate solution and then with water until free from sodium carbonate and halides; m. p. 247–248° with decomposition.

Anal. Calcd. for $C_7H_6O_4NAs$: As, 30.84. Found: As, 30.94.

Summary

The preparation of fifteen arsonic and arsinic acids, ten haloarsines and three arsine oxides has been described.

ANN ARBOR, MICH. RECEIVED SEPTEMBER 18, 1936

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Diarsyls. VIII. Amino and Hydroxydiarsyls[1]

BY F. F. BLICKE AND G. L. WEBSTER[2]

It was to be expected that water-soluble tetraaryldiarsyls could be obtained by the preparation of salts of tetraaryldiarsyls which contained nuclear amino or hydroxyl groups. It has been found that 3,3′,3′′,3′′′-tetra-(aminophenyl)-diarsyl[3] forms a water-soluble hydrochloride and that the sodium salts of 4,4″-dihydroxytetraphenyldiarsyl[4] and 3,3′,3′′,3′′′-tetra-(hydroxyphenyl)-diarsyl[4] are soluble in water.

A study of 2,2″-diaminotetraphenyldiarsyl has shown that this substance, dissolved in benzene, separates from the solution when the latter is shaken with concentrated hydrochloric acid in the form of a crystalline, benzene-insoluble compound. When water is added to the mixture the crystalline product dissolves and the diarsyl is found to be present in the benzene layer. This behavior indicates that the hydrochloride of this diarsyl is hydrolyzed extensively by water.

2,2″-Diaminotetraphenyldiarsyl was prepared by two methods: (a) interaction of 2,2″-diaminotetraphenylarsyl oxide with diphenylarsine, a reaction which yields both 2,2″-diaminotetraphenyldiarsyl and tetraphenyldiarsyl; (b) reaction between 2,2″-diaminotetraphenylarsyl oxide and 2-aminodiphenylarsine.

When diphenylarsine was added to 2,2″-dihydroxytetraphenylarsyl oxide, dissolved in benzene, tetraphenyldiarsyl began to precipitate at once but we were not able to isolate the alkali-soluble 2,2″-dihydroxytetraphenyldiarsyl in crystalline form.

2-Methoxydiphenyliodoarsine, dissolved in benzene, reacted rapidly with molecular silver. Although the reaction product could be obtained only in the form of an oil, the halogen-free material seemed to be 2,2″-dihydroxytetraphenyldiarsyl since it decolorized iodine instantly to yield 2-methoxydiphenyliodoarsine.

3,3″-Dihydroxytetraphenyldiarsyl was formed when 3,3′-dihydroxydiphenylarsinic acid was reduced with hypophosphorous acid. The compound is soluble in alkali and reacts rapidly with oxygen when dissolved in an organic solvent.

When 3,3″-dihydroxytetraphenyldiarsyl was methylated with dimethyl sulfate the corresponding 3,3″-dimethoxydiarsyl was produced. This compound also reacts rapidly with oxygen.

A very limited chemical study of dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl was made by Bertheim.[5] He treated methyl-3-amino-4-hydroxyphenylarsinic acid with hypophosphorous acid, whereupon the crystalline dihypophosphite of the diarsyl precipitated. He analyzed this compound and stated that it irritates the mucous membrane. Upon treatment of the dihypophosphite with hydrochloric acid a water-soluble dihydrochloride was produced. Bertheim concluded his study of this diarsyl with the analysis of this salt.

We prepared the dihypophosphite of dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl in the manner described above, treated the material with sodium hydroxide solution until a clear solution was obtained, acidified the latter with acetic acid and isolated the precipitated diarsyl. The dihydrochloride was prepared from the free base. It was found that this salt, as well as an aqueous, alkaline solution of the diarsyl, absorbed oxygen.

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[1] This paper represents part of a dissertation submitted to the Horace H. Rackham School of Graduate Studies by G. L. Webster in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] University Fellow in the Horace H. Rackham School of Graduate Studies.

[3] Blicke, Oakdale and Oneto, THIS JOURNAL, **56**, 141 (1934).

[4] Blicke and Oneto, *ibid.*, **56**, 685 (1934).

[5] Bertheim, *Ber.*, **48**, 359 (1915).

Experimental Part

The apparatus shown in the accompanying drawing was found to be very useful for the preparation of amino and hydroxy diarsyls. When an aminodiarsyl is precipitated from an acid solution or a hydroxydiarsyl from an alkaline solution the diarsyls tend to separate in a somewhat flocculent state, hence are difficult to wash by decantation. By the use of the modified free radical bulb the product can be filtered by means of the glass filter (Jena filter). A slight pressure from a tank of nitrogen is applied through the side arm attached to the bulb. After filtration the diarsyl is dissolved from the filter plate by a suitable solvent and the solution decanted into the usual type of radical bulb.

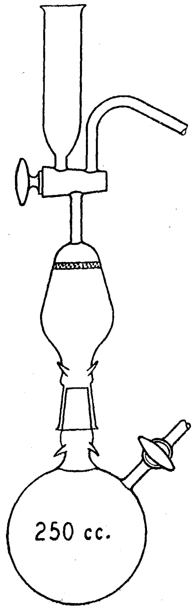

Fig. 1.

2,2″ - Diaminotetraphenyldiarsyl. (a) **From 2,2″-Diaminotetraphenylarsyl Oxide and Diphenylarsine.**—To 3.6 cc. (0.02 mole) of diphenylarsine, washed into a radical bulb filled with nitrogen with 10 cc. of absolute alcohol, there was added 5.0 g. (0.01 mole) of 2,2″-diaminotetraphenylarsyl oxide, dissolved in 10 cc. of alcohol. After twelve hours the alcoholic mother liquor was decanted from the precipitated diarsyls and discarded and the latter washed several times with small amounts of alcohol. The material was dried under diminished pressure, dissolved in 35 cc. of benzene, the solution transferred to a modified radical apparatus (see illustration) and shaken with 25 cc. of hydrochloric acid. The white, crystalline precipitate, the dihydrochloride of the diaminodiarsyl, was filtered, the crystals washed three times with 20 cc. of benzene and the benzene added to the original benzene filtrate which had been collected in a second radical bulb (this solution contained tetraphenyldiarsyl).

The white, crystalline material was shaken with a mixture of 50 cc. of water and 20 cc. of benzene, whereupon the product dissolved in the benzene layer. The aqueous layer was removed, the solvent distilled from the benzene layer under diminished pressure and the crystalline residue dissolved in 10 cc. of hot alcohol. 2,2″-Diaminotetraphenyldiarsyl separated from the cold solution and was then recrystallized from 20 cc. of alcohol; yield 2.3 g.

The diarsyl is very soluble in benzene, acetone and ether and the solutions rapidly turn dark red when exposed to air.

Dissolved in bromobenzene 0.860 g. of the diarsyl absorbed 30 cc. (N. T. P.) of oxygen in one minute.

In order to isolate the tetraphenyldiarsyl the solvent was removed from the benzene solution in the second radical bulb, the crystalline residue washed with alcohol and then recrystallized from 200 cc. of this solvent; yield 2.6 g.; m. p. 129–131° in a sealed tube filled with nitrogen.[6]

The rather peculiar behavior of the hydrochloride of the diaminodiarsyl was studied again after the diarsyl had been isolated. A sample of the diarsyl, dissolved in benzene, was shaken with hydrochloric acid, whereupon a white, crystalline precipitate appeared. After the addition of water the precipitate disappeared and the diarsyl was recovered from the benzene layer. Apparently the hydrochloride is hydrolyzed very extensively by water.

When 0.57 g. of the diaminodiarsyl was dissolved in 1 cc. of acetic anhydride, heated for thirty minutes, cooled and treated with water the gummy diacetyl derivative was obtained. This material was dissolved in 2 cc. of acetic acid and treated with 0.3 g. of iodine, dissolved in benzene. The iodine was decolorized instantly and after removal of the solvents 1 g. of crude 2-acetylaminodiphenyliodoarsine[7] was obtained; m. p. 147–148° after recrystallization from acetic acid.

(b) **From 2,2″-Diaminotetraphenylarsyl Oxide and 2-Aminodiphenylarsine.**—From a mixture of 2.3 g. of 2-aminodiphenylarsine, dissolved in 20 cc. of alcohol, and 2.5 g. of 2,2″-diaminotetraphenylarsyl oxide, dissolved in 30 cc. of the same solvent, there had precipitated, at the end of twenty-four hours, 2.1 g. of the diaminodiarsyl; m. p. 133–135° after recrystallization from 50 cc. of alcohol.

3,3″-Diaminotetraphenyldiarsyl.—Ammonia water was added to 4.5 g. of 3-aminodiphenylchloroarsine hydrochloride,[7] dissolved in water, the gummy precipitate extracted with ether, the ether solution poured into a radical bulb and the solvent removed. The colorless, oily 3,3″-diaminotetraphenylarsyl oxide was dissolved in 20 cc. of 50% hypophosphorous acid which contained four drops of hydriodic acid. The mixture was heated at 70° for three hours and after twelve hours made alkaline with 10% sodium hydroxide solution, the precipitate washed with water, dissolved in 100 cc. of alcohol and filtered into a second radical bulb. After distillation of about 75 cc. of alcohol the diarsyl separated in crystalline condition.

Dissolved in acetophenone 1.1550 g. of the diarsyl absorbed 47 cc. (N. T. P.) of oxygen in thirty seconds; calcd. amount 53 cc.

A mixture of 1.2 g. of the diarsyl, 15 cc. of acetone and 3 cc. of acetic anhydride was heated for one hour and the solvents removed. Since the residue would not crystallize the acetylated diarsyl was treated with 0.66 g. of iodine, dissolved in 10 cc. of alcohol. The iodine color disappeared instantly. The alcohol was removed and the residue rubbed under 3 cc. of acetic acid whereupon the product crystallized; this compound, 3-acetylaminodiphenyliodoarsine,[7] melted at 146–147° after recrystallization from acetic acid; mixed m. p. 146–147°.

3,3″-Dihydroxytetraphenyldiarsyl.—A mixture of 5.8 g. of 3-hydroxydiphenylarsinic acid, 10 cc. of alcohol, two drops of hydriodic acid and 20 cc. of 50% hypophosphorous acid in a modified radical bulb was heated in a bath at 70° for three hours. To the cold solution, 200 cc. of water was added slowly. The diarsyl precipitated as a liquid which soon became crystalline. The liquid was decanted, the diarsyl washed thoroughly with water, dried under reduced pressure, dissolved in hot benzene, the solution filtered, cooled, and the diarsyl precipitated by the addition of 150 cc. of petroleum ether (90–100°); yield 3.6 g.

The hydroxydiarsyl is soluble in alkali: 0.417 g. of the

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[6] Blicke, Weinkauff and Hargreaves [THIS JOURNAL, **52**, 782 (1930)] reported 129–130°.

[7] Blicke and Webster, *ibid.*, **59**, 536 (1937).

material dissolved in a mixture of 0.14 g. of sodium hydroxide and 10 cc. of water. Upon the addition of hydrochloric acid the diarsyl was recovered unchanged. It is also soluble in benzene and very soluble in alcohol and acetone. Dissolved in acetophenone the diarsyl absorbed oxygen rapidly.

3,3″-Dimethoxytetraphenyldiarsyl.—The 3,3″-dihydroxytetraphenyldiarsyl, obtained from 5.8 g. of 3-hydroxydiphenylarsinic acid, was dissolved in a mixture of 10 cc. of 40% sodium hydroxide solution and 25 cc. of water and shaken with 3 cc. of dimethyl sulfate. The methylation process was repeated with 20 cc. of 40% sodium hydroxide solution and 6 cc. of dimethyl sulfate. The mixture, from which the methoxy derivative had settled as a gum, was heated for some time; when cooled, the product crystallized. It was washed with alkali and water, dissolved in 35 cc. of benzene and the solution filtered into a second radical bulb. The benzene was removed and the diarsyl recrystallized from 20 cc. of alcohol; yield 3.8 g.

A solution obtained from 1.28 g. of the diarsyl and 20 cc. of acetophenone absorbed 52 cc. (N. T. P.) of oxygen in thirty seconds; calcd. 55 cc.

Dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl.—A solution prepared from 4.6 g. of methyl-3-amino-4-hydroxyphenylarsinic acid and 30 cc. of 50% hypophosphorous acid was introduced into the modified radical bulb and a mixture of 0.5 cc. of hydriodic acid and 20 cc. of hypophosphorous acid added. After about thirty minutes the precipitated diarsyl hypophosphite[5] (p. 358) was filtered and the material washed three times with 50-cc. portions of water. It was then dissolved in a hot alkaline solution, prepared from 15 g. of sodium hydroxide (70%) and 50 cc. of water, and the hot solution acidified to phenolphthalein with 25% acetic acid. The pure white mat of crystalline product was filtered, washed free from acid with water and then washed with 50 cc. of acetone. The product was washed from the filter plate into the bulb of the apparatus with the aid of a small amount of acetone, the acetone removed by distillation under reduced pressure and the crystalline diarsyl dried at 80–85° for four hours under reduced pressure.

In order to obtain the diarsyl dihydrochloride 2.5 g. of the diarsyl was dissolved in a mixture of 27 cc. of 0.5 *N* hydrochloric acid and 75 cc. of methyl alcohol and the solvents removed at 35° under reduced pressure. The residue was dried at 85–90° under reduced pressure for six hours and isolated in a carbon dioxide atmosphere; m. p. 168–170° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{14}H_{20}O_2N_2Cl_2As$: As, 31.95; Cl, 15.12. Found: As, 31.44; Cl, 14.81.

TABLE I

DIARSYLS

	M. p., °C.[a]	Formula	As, % Calcd.	As, % Found
2,2″-Diamino-tetraphenyl	133–134	$C_{24}H_{22}N_2As_2$	30.71	30.76
3,3″-Diamino-tetraphenyl	146–148	$C_{24}H_{22}N_2As_2$	30.71	30.39
3,3″-Dihydroxy-tetraphenyl	134–136	$C_{24}H_{20}O_2As_2$	30.59	30.24
3,3″-Dimethoxy-tetraphenyl	98–99	$C_{26}H_{24}O_2As_2$	28.92	28.86
Dimethyl-di-(3-amino-4-hydroxyphenyl)	184–185	$C_{14}H_{18}O_2N_2As_2$	37.84	37.59

[a] Determined in a sealed tube filled with nitrogen.

2-Aminodiphenylarsine.—A solution of 46 g. of 2-aminodiphenylarsinic acid[8] in 280 cc. of hydrochloric acid was placed in a three-liter, three-necked flask the necks of which were fitted with a mercury trap, through which hydrogen could escape, a mechanical stirrer and a wide-stemmed funnel. The stem of the funnel was connected to the flask by means of a short piece of rubber tubing which could be opened and closed with the aid of a pinch clamp. The mixture was stirred and 90 g. of dry, amalgamated zinc dust was added during the course of two hours. A dark colored, sandy precipitate formed. After five hours 100 cc. of hydrochloric acid was added and the mixture stirred for twelve hours longer; 500 cc. of 40% sodium hydroxide solution and 400 cc. of ether, previously saturated with nitrogen, were then added. The ether layer was siphoned into a nitrogen-filled separatory funnel which contained soda-lime. The dry ether solution was allowed to flow, very slowly, into a small Claisen distillation flask heated on a steam-bath. After removal of the ether the arsine was distilled; b. p. 218–220° under 35 mm. pressure. The arsine absorbs oxygen extremely rapidly and becomes deep red-brown in color.

When 5.81 g. of the arsine, dissolved in benzene, was allowed to oxidize in air there were obtained 1.43 g. of 2-aminodiphenylarsinic acid and 4.53 g. of 2,2″-diaminotetraphenylarsyl oxide.

Summary

The preparation and properties of 2,2″-diamino-, 3,3″-diamino-, 3,3″-dihydroxy- and 3,3″-dimethoxytetraphenyldiarsyl as well as of dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl and 2-aminodiphenylarsine have been described.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 18, 1936

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[8] Kalb, *Ann.*, **423**, 60 (1921).

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

Keto Ethers. II. α-1,3-Dichloroisopropoxyethyl Alkyl Ketones[1]

BY BRUCE B. ALLEN WITH HENRY R. HENZE

Continuing the investigation in this Laboratory on aliphatic compounds of bifunctional type,[2] we have now studied the utilization of glycerol 1,3-dichlorohydrin in the preparation of chlorinated keto ethers. With but very few exceptions, only the simpler, monohydric alcohols have been condensed with the unsubstituted aliphatic aldehydes of low molecular weight, or with trichloroacetaldehyde, according to Henry's[3] method for synthesizing α-chloro ethers. The first successful utilization of a substituted alcohol in this chloro ether synthesis was that of Stappers,[4] in 1905, who effected the condensation of propylene chlorohydrin with formaldehyde, even though aqueous formalin solution was used as a source of the aldehyde. Somewhat later, Grignard and Purdy,[5] using ethylene chlorohydrin and paraldehyde, were able to produce α-chloroethyl β'-chloroethyl ether. However, the attempts of Farren, Fife, Clark and Garland[6] to cause trioxymethylene to interact with glycol and glycerol, respectively, led to no satisfactory results. Although these investigators were convinced that condensation had occurred, they were unable to isolate any pure products from the reaction mixtures. Finally, Blanchard[7] has reported the only other attempt at reaction of an aldehyde with a chlorohydrin, he having obtained 1,3-dichloroisopropyl chloromethyl ether by the action of hydrogen chloride on a mixture of trioxymethylene and glycerol 1,3-dichlorohydrin.

Following the work of Gauthier,[8] by which it was possible to convert α-chloro ethers into the corresponding alkoxy nitriles by heating the former with either cuprous or mercuric cyanides, there have been, from time to time, numerous references made to the preparation and characterization of compounds of this type. Apparently, however, no attempts have been made to apply this reaction to the synthesis of substituted alkoxy nitriles, *e. g.*, chloroalkoxy nitriles from polyhalogenated ethers. Likewise, since chloroalkoxy nitriles were unknown prior to this investigation, there necessarily have been no chloroalkoxy ketones obtained by the procedure of Béhal and Sommelet,[9] in which they found it possible to adapt Blaise's[10] modification of the Grignard reaction in the formation of keto ethers from alkoxy nitriles.

Glycerol 1,3-dichlorohydrin has now been caused to react with paraldehyde to form 1,3-dichloroisopropyl α-chloroethyl ether. This new trichloro ether has been converted into α-1,3-dichloroisopropoxypropionitrile, the latter representing the first example of a chloroalkoxy nitrile to be prepared. From this nitrile there has been obtained, by means of the Grignard reaction, a series of dichloroalkoxy alkyl ketones.

The Hoesch[11] test, as modified by Howells and Little,[12] has been proposed as a micro method for the identification of alkyl nitriles. The condensation of α-1,3-dichloroisopropoxypropionitrile with phloroglucinol has been investigated, with the result that the proposed test appears to be of no value for the recognition of chloroalkoxy nitriles.

Experimental

1,3-Dichloroisopropyl α-Chloroethyl Ether.—Dry hydrogen chloride was passed into a well-stirred mixture of 973 g. (7.55 moles) of glycerol 1,3-dichlorohydrin, prepared by the method of Conant and Quayle,[13] and 502 g. (3.8 moles) of paraldehyde contained in a flask cooled by an ice–salt bath. Saturation was attained in five hours, the mixture separating into two layers. The crude chloro ether layer, weighing 1646 g., was dried over calcium chloride and distilled under diminished pressure. Redistillation at 18 mm. pressure yielded 1142 g. (79.2% of the theoretical) of 1,3-dichloroisopropyl α-chloroethyl ether boiling at 89–90° (corr.). The colorless, oily liquid has a pleasant odor and in contact with air undergoes rather rapid decomposition with the evolution of hydrogen chloride and the deposition of a black, gummy mass: d^{20}_4 1.2864; n^{20}_D 1.4711; M_R calcd., 41.53; M_R found, 41.60; γ^{20} 34.44 dynes/cm.; P calcd., (Sugden's atomic constants) 360.8;

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[1] From the thesis of Bruce B. Allen for the M.A. degree, August, 1936.

[2] Henze and Rigler, THIS JOURNAL, **56**, 1350 (1934).

[3] Henry, *Bull. soc. chim.*, [2] **44**, 458 (1885).

[4] Stappers, *Rec. trav. chim.*, **24**, 256 (1905).

[5] Grignard and Purdy, *Bull. soc. chim.*, **31**, 982 (1922).

[6] Farren, Fife, Clark and Garland, THIS JOURNAL, **47**, 2412 (1925).

[7] Blanchard, *Bull. soc. chim.*, **39**, 1119 (1926).

[8] Gauthier, *Compt. rend.*, **143**, 831 (1906).

[9] Béhal and Sommelet, *ibid.*, **138**, 89 (1904).

[10] Blaise, *ibid.*, **132**, 38 (1901).

[11] Hoesch, *Ber.*, **48**, 1122 (1915).

[12] Howells and Little, THIS JOURNAL, **54**, 2451 (1932).

[13] Conant and Quayle, "Organic Syntheses," John Wiley & Sons, Inc., New York, Vol. II, 1922, p. 29.

TABLE I

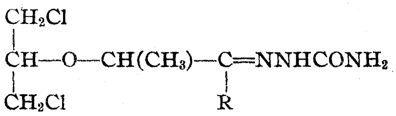
KETO ETHERS DERIVED FROM GLYCEROL 1,3-DICHLOROHYDRIN

Formula	B. p. °C.	B. p. Mm.	Density d^{20}_4	Refractive index, $n^{20}D$	Surface tension γ^{20}, dynes	Free surface energy $\gamma\ (m/d)^{2/3}$ ergs	Yield, %
$(CH_2Cl)_2CHOCH(CH_3)COCH_3$	105–106	5	1.1986	1.4640	35.81	1086.5	51.4
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_3$	117	7–7.5	1.1691	1.4636	34.97	1139.7	79.5
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_2CH_3$	127.5	5	1.1381	1.4627	33.85	1169.2	66.1
$(CH_2Cl)_2CHOCH(CH_3)COCH(CH_3)_2$	124–125.5	12	1.1359	1.4613	33.66	1163.1	47.4
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_2CH_2CH_3$	136–136.5	6	1.1140	1.4625	32.90	1205.4	62.7
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH(CH_3)_2$	127–128	5–6	1.1096	1.4608	31.75	1166.4	53.3
$(CH_2Cl)_2CHOCH(CH_3)COCH(CH_3)CH_2CH_3$	129–130	5	1.1167	1.4624	32.90	1203.5	19.9
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_2CH_2CH_2CH_3$	148.5–149	5–5.5	1.0932	1.4630	32.59	1260.9	75.9
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_2CH(CH_3)_2$	143–144	5	1.0926	1.4627	31.89	1234.2	44.0
$(CH_2Cl)_2CHOCH(CH_3)COC_6H_2(OH)_3$	175.5	(m. p.)	....	....	...	....	32.5

Formula	Chlorine, % Calcd.	Chlorine, % Found	Molecular refraction Calcd.	Molecular refraction Found	ΔM_R	Parachor Calcd.	Parachor Found	ΔP
$(CH_2Cl)_2CHOCH(CH_3)COCH_3$	35.63	35.56	45.91	45.82	−0.09	410.6	406.2	− 4.4
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_3$	33.30	33.18	50.53	50.24	− .29	449.6	443.1	− 6.5
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_2CH_3$	31.23	31.24	55.15	54.92	− .22	488.6	481.2	− 7.4
$(CH_2Cl)_2CHOCH(CH_3)COCH(CH_3)_2$	31.23	31.49	55.15	54.87	− .28	488.6	481.6	− 7.0
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_2CH_2CH_3$	29.42	29.27	59.77	59.55	− .22	527.6	518.3	− 9.3
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH(CH_3)_2$	29.42	29.38	59.77	59.59	− .18	527.6	515.7	−11.9
$(CH_2Cl)_2CHOCH(CH_3)COCH(CH_3)CH_2CH_3$	29.42	29.57	59.77	59.39	− .38	527.6	517.0	−10.6
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_2CH_2CH_2$-$CH_3$	27.80	27.63	64.39	64.26	− .13	566.6	557.5	− 9.1
$(CH_2Cl)_2CHOCH(CH_3)COCH_2CH_2CH(CH_3)_2$	27.80	27.79	64.39	64.26	− .13	566.6	554.8	−11.8
$(CH_2Cl)_2CHOCH(CH_3)COC_6H_2(OH)_3$	22.95	23.20	...	...	....	...	...	....

TABLE II

SEMICARBAZONES OF α-1,3-DICHLOROISOPROPOXYETHYL KETONES



$$\begin{array}{l} CH_2Cl \\ | \\ CH{-}O{-}CH(CH_3){-}\underset{\displaystyle R}{\underset{|}{C}}{=}NNHCONH_2 \\ | \\ CH_2Cl \end{array}$$

α-1,3-Dichloroisopropoxyethyl	R	M. p., °C. (corr.)	Nitrogen, % Calcd.	Nitrogen, % Found
-Methyl ketone	$—CH_3$	110.5	16.41	16.28
-Ethyl ketone	$—CH_2CH_3$	131.5–132	15.56	15.42
-*n*-Propyl ketone	$—CH_2CH_2CH_3$	114.5	14.79	14.71
-*n*-Butyl ketone	$—CH_2CH_2CH_2CH_3$	94.8	14.10	14.16
-*n*-Amyl ketone	$—CH_2CH_2CH_2CH_2CH_3$	108.6	13.46	13.44
-iso-Amyl ketone	$—CH_2CH_2CH(CH_3)_2$	111.5	13.46	13.61
Semicarbazone of α-1-iodo-3-chloroisopropoxyethyl methyl ketone		123–124	12.09	11.96

P found, 360.5. *Anal.* Calcd. for $C_5H_9Cl_3O$: Total Cl, 55.56. Found: Cl, 55.51, 55.07 (by Carius method). α-Cl content calcd., 18.52. Found: Cl, 18.15, 18.29 (by direct determination with aqueous silver nitrate solution).

α-1,3-Dichloroisopropoxypropionitrile.—The method of Gauthier[8] was adapted: 500 g. (2.61 moles) of 1,3-dichloroisopropyl α-chloroethyl ether, diluted with 125 cc. of anhydrous benzene, was added dropwise over a period of one hour to 250 g. of dry cuprous cyanide. Reaction was evidenced by the evolution of sufficient heat to occasion refluxing of the benzene. The mixture was stirred and heated on a steam-bath for three hours. After removal of the mixed cuprous salts by filtration, the benzene was distilled and the residual liquid fractionated under diminished pressure; yield, 232 g. (48.8%); b. p. 99° (corr.)/4 mm.; d^{20}_4 1.2259; $n^{20}D$ 1.4643; M_R calcd., 41.10; M_R found, 40.99; γ^{20} 37.77 dynes/cm.; P calcd., 370.4; P found, 368.0.

Anal. Calcd. for $C_6H_9Cl_2NO$: Cl, 39.03; N, 7.69. Found: Cl, 39.24; N, 7.64.

Preparation of α-1,3-Dichloroisopropoxyethyl Alkyl Ketones.—Sommelet's[14] method for preparing alkoxy ketones from alkoxy nitriles was applied successfully to the synthesis of dichloroalkoxy ketones, except in the case of the first member of the series. In general, the appropriate alkylmagnesium halide was prepared under anhydrous conditions and treated with the α-1,3-dichloroisopropoxypropionitrile. The reaction product, after standing overnight, was decomposed by addition of ice-cold, dilute hydrochloric acid, and the yellow colored ether solution was separated,

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[14] Sommelet, *Ann. chim. phys.*, [8] 9, 484 (1906).

dried over calcium chloride, and fractionated under a pressure of 5 mm. until sufficiently purified. The keto ethers were obtained as colorless oils having faint, slightly rancid odors which became more intense with age; unless highly purified the compounds darkened to a deep yellow color upon standing in contact with air. All of these oils were found to be insoluble in water, but readily miscible with organic solvents such as alcohol, ether, acetone, chloroform, benzene and petroleum ether.

An attempt to prepare the simplest member of the series by interaction of α-1,3-dichloroisopropoxypropionitrile and methylmagnesium iodide resulted in the formation of a reddish-brown oil which decomposed on distillation below 5 mm. pressure. From this oil there was formed a semicarbazone which melted with decomposition at 123–124° (corr.) after recrystallization from a benzene–petroleum ether mixture. Analysis of the semicarbazone indicated there had been partial replacement of chlorine by iodine during the Grignard reaction, with production of α-1-chloro-3-iodoisopropoxyethyl methyl ketone. Effort was made to regenerate this ketone from its semicarbazone, but the resulting liquid decomposed on attempted distillation under diminished pressure. For this semicarbazone the following data were obtained. *Anal.* Calcd. for $C_8H_{15}ClIN_3O_2$: Cl, 10.20; I, 36.52; N, 12.09. Found: Cl, 9.99; I, 36.30; N, 11.96.

The desired dichloro ketone was secured by utilizing methylmagnesium bromide instead of the iodide. Difficulty was also encountered in endeavors to synthesize the *t*-butyl member of the series. Initial trials were made using *t*-butylmagnesium bromide, but very nearly all of the chloroalkoxy nitrile was recovered unchanged. Following the suggestion of Gilman and Zoellner,[15] that better yields of Grignard reagent are obtained by using *t*-butyl chloride rather than the bromide, renewed attempts were made using the alkylmagnesium chloride, but here, too, no keto ether was obtained.

Semicarbazones, easily prepared and readily purified, useful as a further means of identifying the keto ethers, were formed from all the ketones containing the normal alkyl structure and, also, from α-1,3-dichloroisopropoxyethyl isoamyl ketone. Since these ketones which formed solid semicarbazones did so with such rapidity and in such good yields, failure to obtain such solids in the instances of the isobutyl, *s*-butyl and *s*-propyl α-1,3-dichloroisopropoxyethyl ketones must be attributed to steric hindrance resulting from alkyl substitution in the positions alpha or beta to the carbonyl group.

The Hoesch[11] test, as proposed by Howells and Little[12] as a micro method for identifying alkyl cyanides, was employed in the formation of a new dichloroalkoxyalkyl trihydroxyphenyl ketone. Although the amounts of materials used (0.04 mole) were considerably larger than those deemed adequate by Howells and Little, the yield of purified ketone was scarcely more than enough for simple characterization and analysis.

Boiling points were taken with calibrated thermometers and the properly corrected values are reported for the liquid keto ethers. Likewise, the melting points of the trihydroxyphenyl ketone and of the seven semicarbazones prepared are corrected values. Surface tensions were measured by means of Cassel's[16] precision capillarimeter at 20°. Densities were determined by means of a Sprengel tube weighing 1.2734 g. and calibrated to contain 2.1316 g. of distilled water at 4°. The data resulting from the determination of physical constants, the values derived from these data by calculation, and such information as was obtained through analysis of these keto ethers have been tabulated in Table I. Table II is devoted to the data resulting from the study of the semicarbazones of the dichloroalkoxy ketones.

Summary

1. The series of β',β''-dichloro-α-chloroalkyl ethers has been extended by the synthesis of 1,3-dichloroisopropyl α-chloroethyl ether. The latter has been converted into α-1,3-dichloroisopropoxypropionitrile, the first chloroalkoxy nitrile yet prepared.

2. Nine examples of a new type of chlorinated keto ether have been obtained. In this series of dichloroisopropoxyethyl alkyl ketones, the normal, iso- and secondary alkyl types are represented; the tertiary alkyl type could not be synthesized by means of the Grignard reaction from the nitrile.

In an attempted preparation of α-1,3-dichloroisopropoxyethyl methyl ketone from methylmagnesium iodide, replacement of chlorine was observed, and the iodochloroalkoxy ketone formed was subsequently identified by means of its semicarbazone.

3. Semicarbazones, useful in the identification of the keto ethers, were obtained from each of the normal alkyl homologs and, as well, from the isoamyl member of the series. Failure of the secondary propyl, secondary butyl, and isobutyl ketones to form solid semicarbazones may be attributed to steric hindrance.

4. The Hoesch test, as modified by Howells and Little, apparently is valueless as a micro method for the identification and recognition of chloroalkoxy nitriles.

5. For the series of compounds included in this investigation, the parachor was found to be less sensitive than the molecular refraction as an index to purity.

AUSTIN, TEXAS RECEIVED JANUARY 12, 1937

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[15] Gilman and Zoellner, THIS JOURNAL, **50**, 425 (1928).

[16] Cassel, *Chem.-Ztg.*, **53**, 479 (1929).

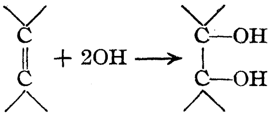
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 149]

The Photochemical Addition of Hydrogen Peroxide to the Double Bond

BY NICHOLAS A. MILAS, PHILIP F. KURZ[1] AND WILLIAM P. ANSLOW, JR.[2]

Considerable spectroscopic evidence[3] has recently accumulated to show that light in the region of about 3000 Å. causes the dissociation of hydrogen peroxide into two hydroxyl radicals. However, very little direct chemical evidence exists in favor of the formation of these radicals. Our interest in the hydroxylation of unsaturated substances[4] led us to devise experiments whereby free hydroxyl radicals, produced either by the photochemical dissociation of hydrogen peroxide or by the dissociation of water or hydrogen peroxide in the field of an electrodeless discharge,[5] could be made to react with unsaturated substances to form hydroxylated products in which the hydroxyl groups retain their identity. Essentially, the reactions may be illustrated as follows

$$\mathrm{HOOH} + h\nu \longrightarrow 2\mathrm{OH} \qquad (1)$$



(2)

Since the life of these radicals is of short duration, the unsaturated substances were either mixed directly with their precursor, hydrogen peroxide, and the mixture exposed to ultraviolet radiation, as in the case of the present experiments, or allowed to meet the hydroxyl radicals in the immediate vicinity of, but not within, the field of the electrodeless discharge. Using the first method, we succeeded in producing glycerol from allyl alcohol, dihydroxybutyric acid from crotonic acid, mesotartaric acid from maleic acid, and diethyl mesotartrate from diethyl maleate. It was not possible to produce these dihydroxy substances when the mixtures were allowed to stand in the dark, and their production therefore is attributed to the presence of hydroxyl radicals in the photochemical reaction. That free hydroxyl radicals react in this fashion was also shown by the second method in which ethylene glycol was produced from ethylene.[5]

Experimental Part

A Cooper–Hewitt mercury vapor lamp was used in all of our experiments at a distance of 50 cm. from the quartz vessel containing the reaction mixtures. The latter was surrounded with an aluminum reflector in such a way that maximum utilization of the necessary light was effected. To ensure a greater surface, shaking of the reaction vessel during radiation was found beneficial in some experiments. An electric fan was allowed to play on the reaction vessel, thereby preventing a rise of temperature above that of the room.

The hydrogen peroxide used in many of the experiments was prepared either by the method of Rice, Reiff and Kilpatrick,[6] or that of Hurd and Puterbaugh,[7] and appropriate dilutions were made from this. Parallel experiments of the same concentration of the reactants were conducted in the presence and absence of ultraviolet light and the rate of the disappearance of hydrogen peroxide was determined in each case. Preliminary experiments were first made in 70 and 30% solutions of hydrogen peroxide, respectively, with maleic and crotonic acids, but the oxidation was much too destructive to permit isolation of the hydroxy compounds. Best results were finally obtained in a solution of about 10% hydrogen peroxide. In the dark, the reactions were not only slow, but in no case were we able to isolate the dihydroxy compounds. The 70% solution of hydrogen peroxide oxidized maleic acid rapidly in the dark, but attempts to isolate mesotartaric acid were not successful.

Glycerol from Allyl Alcohol.—Ten grams of allyl alcohol was mixed in a quartz flask with a solution of 10% hydrogen peroxide in the molal ratio of 1:1.05, and the mixture exposed to ultraviolet light under shaking at about 100 strokes per minute. At the end of one hundred and sixty-eight hours, the mixture had lost 89% of its peroxide content while the sample in the dark remained the same. To separate the glycerol formed, the mixture was subjected to fractional distillation and the fraction (6.8 g.) boiling at 287–289° collected. This corresponds to a yield of 43% based on the amount of alcohol used. Since there was no carbon dioxide evolved during the reaction and most of the unreacted allyl alcohol recovered, the yield of glycerol was actually considerably higher. It may also be seen that for every mole of hydrogen peroxide reacted there was approximately one mole of peroxide decomposed to oxygen and water.

Dihydroxybutyric Acid from Crotonic Acid.—Ten grams of crotonic acid (Eastman Kodak Company) was mixed in a quartz flask with 70 cc. of 5.8% solution of hydrogen peroxide and the mixture exposed to ultraviolet light while

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[1] B.S. Thesis, M. I. T., 1935.

[2] B.S. Thesis, M. I. T., 1936.

[3] Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1371 (1929); von Elbe, *ibid.*, **55**, 62 (1933); Rodebush and Wahl, *J. Chem. Phys.*, **1**, 696 (1933); Oldenberg, *ibid.*, **3**, 266 (1935); Frost and Oldenberg, *ibid.*, **4**, 642, 781 (1936); Kondratjew and Zinskin, *Acta Physicochim. U. R. S. S.*, **5**, 301 (1936).

[4] Milas and Sussman, THIS JOURNAL, **58**, 1302 (1936).

[5] Milas, Stahl and Dayton, unpublished results.

[6] Rice, Reiff and Kilpatrick, THIS JOURNAL, **48**, 3019 (1926).

[7] Hurd and Puterbaugh, *ibid.*, **52**, 950 (1930).

shaking at about 100 strokes per minute. At the end of one hundred and seventy hours, the mixture had lost 77% of its peroxide content while the mixture in the dark remained the same. The products were separated following the method of Braun.[8] The unreacted crotonic acid was separated by extraction with chloroform and the residual solution concentrated at room temperature under reduced pressure. The viscous sirup thus obtained was further dried for twenty-four hours in a vacuum oven at 40° and at a pressure of 2 mm. The highly viscous sirup (4.2 g.) thus obtained corresponded to a 30% yield of dihydroxybutyric acid based on the total amount of crotonic acid used. Two samples of this were then titrated against a standard alkali and gave an average neutralization equivalent of 119 which is in close agreement with the calculated value of 120 for dihydroxybutyric acid.

A small amount of destructive oxidation also took place since both carbon dioxide and acetaldehyde were detected in the reaction mixture.

Mesotartaric Acid from Maleic Acid.—Several experiments were carried out with maleic acid using concentrated hydrogen peroxide solutions, but in all cases the oxidation was too destructive, yielding copious quantities of carbon dioxide and products not easily identifiable. Finally, 10 g. of maleic acid was dissolved in 53 cc. of 5.8% hydrogen peroxide solution and the latter exposed to ultraviolet light under similar conditions as in the previous cases. After one hundred and twenty-two hours, the solution had lost about 88% of its original strength of hydrogen peroxide while the dark reaction lost only 12% of its strength. When the products of the photochemical reaction were worked up following the method of Milas and Sussman,[4] a yield of 4.65% of mesotartaric acid was obtained. In another experiment in which the reaction was allowed to proceed only for thirty hours, the yield of mesotartaric acid was 9% of the total maleic acid used. The calcium salt of the mesotartaric acid obtained was purified by reprecipitation and dried in an oven for twenty-four hours at 105°.

Anal. Calcd. for $C_4H_4O_6Ca$: Ca, 21.28. Found: Ca, 21.05, 21.09, 21.52.

The dark reaction yielded no mesotartaric acid. This observation is in accordance with the findings of Hatcher and Mueller.[9]

Mesotartaric Acid from Diethyl Maleate.—The diethyl maleate was prepared by refluxing for four hours a mixture of 100 g. of maleic acid, 250 cc. of absolute ethyl alcohol and 20 g. of sulfuric acid (sp. gr. 1.84), then cooling and pouring the mixture into cold water. The ester was separated, washed with five successive 40-cc. portions of saturated sodium bicarbonate solution and fractionated; the fraction boiling from 219 to 220° (uncorr.) was collected and used in our experiments. The b. p. of this ester is given in the literature[10] as 225° (corr.). Inasmuch as this ester is insoluble in water, anhydrous solutions of hydrogen peroxide in ether or tertiary butyl alcohol were mixed with it in such proportions that the molal ratio of the ester to hydrogen peroxide was 1:1.05. The solvents were then removed under reduced pressure and the residual mixture irradiated as before. At the end of one hundred and twenty-two hours, the reaction mixture was hydrolyzed by refluxing with a solution of 10% alcoholic potash. The alcohol was then removed by distillation, the residue neutralized with dilute hydrochloric acid and the resulting solution made ammoniacal. From this, the mesotartaric acid was precipitated as calcium mesotartrate. A yield of 21.7% calculated as diethyl mesotartrate was obtained. The amount of destructive oxidation, as judged by the amount of carbon dioxide produced, was considerably less than in the case of maleic acid.

Summary

1. It has been shown that hydrogen peroxide, under the influence of ultraviolet light, reacts with double bonded compounds to form the corresponding glycols.

2. Glycerol, dihydroxybutyric acid, mesotartaric acid and diethyl mesotartrate have been obtained from allyl alcohol, crotonic acid, maleic acid and diethyl maleate, respectively.

3. The formation of glycols, in the present case, is assumed to take place through the addition to the double bond of free hydroxyl radicals which are formed by the dissociation of hydrogen peroxide under the influence of ultraviolet light.

Cambridge, Mass. Received February 1, 1937

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[8] Braun, This Journal, **51**, 228 (1929).

[9] Hatcher and Mueller, *Can. J. Research*, **3**, 291 (1930).

[10] Anschütz, *Ber.*, **12**, 2283 (1879).

[CONTRIBUTION FROM THE NEW JERSEY AGRICULTURAL EXPERIMENT STATION]

Lactic Acid Production by Species of Rhizopus[1]

BY SELMAN A. WAKSMAN AND I. J. HUTCHINGS

Although the capacity of forming lactic acid is not widespread among the fungi, it seems to be definitely established that various species belonging to the genus *Rhizopus* are capable of producing this acid from a variety of carbohydrates, including glucose, maltose, sucrose, dextrin and starch. According to Saito,[2] inulin, lactose and sucrose cannot be used as a source of acid; Kanel[3] found, however, that the last carbohydrate is readily utilized. The presence of calcium carbonate is essential for the formation of appreciable quantities of the acid. Ammonium salts or compounds which produce ammonia, such as urea, are preferable to nitrates.

The nature and yield of the lactic acid vary considerably, depending largely upon the specific nature of the organism, including strain specificity, and upon the conditions of cultivation. Saito obtained only a low yield of the levo-rotatory form of the acid; Kanel, however, reported a yield, both from sugar and from starch, of 40% of the *d*-form; the period of incubation was twenty days. Ward, *et al.*,[4] also found that 32 to 62% of sugar was transformed into *d*-lactic acid in sixteen days.

Practically all the fungi capable of producing lactic acid from carbohydrates have been found among the *Mucorales*, chiefly in the genus *Rhizopus*. The only other exception so far reported was found to be a species of *Monilia*.[5] Saito employed in his investigations *Rh. chinensis*. According to Ehrlich,[6] *Rh. nigricans* and *R. tritici* are capable of bringing about the formation of lactic acid. Takahashi[7] used four different strains of *Mucor*. The organism employed by Kanel was *Rh. japonicus*, or a closely related form; Ward, *et al.*, worked with *Rh. oryzae* and *Rh. arrhizus*. When the incubation period is prolonged more than twenty days, the concentration of the lactic acid was shown[3] to be gradually reduced, and other acids, notably fumaric, are formed.

Experimental

In the study of decomposition of plant materials in composts and in soil, a culture of *Rhizopus*, designated as MX, was isolated, which had the capacity of producing, from various carbohydrates large quantities of lactic acid. A comparison was later made of several strains of *Rhizopus* kept in the culture collection, and another organism, No. 36, was selected. The two organisms varied in cultural appearance, especially in the rapidity of spore formation and in the yields of lactic acid. MX was closely related to *Rh. nodosus* or *Rh. arrhizus*. The No. 36 was morphologically very similar to MX.

Several preliminary experiments, using glucose as a source of carbon, were carried out in order to determine the nature of the acid produced. It was soon found that, during the early stages of the growth of the organism, namely, between three and fifteen days, the acid is almost exclusively lactic acid. This was demonstrated by the precipitation of the calcium salt of the acid with alcohol and analysis of the salt. However, after fifteen to twenty days' growth, the lactic acid was transformed slowly to lower acids (fumaric?), as shown by the increase in the calcium content of the salt. It was felt, therefore, that when the determinations were made in cultures only ten to eighteen days old, the calculation of the lactic acid equivalent of the calcium in the salt did not involve any large error. This checked well with the organic matter content of the culture solution, which, after all the sugar had been consumed, was due almost entirely to the acid produced.

Once the nature of the acid was established, a series of experiments was carried out to determine the nutrient requirements of the organisms and especially the acid production from different carbohydrates, under different conditions of culture.

In a preliminary experiment it was found that during the growth of the organism MX in a 5% glucose solution, with ammonium sulfate as a source of nitrogen, the reaction was usually changed, within three days' growth at 28°, from *p*H 7.4 to 4.0 or 4.1. Little lactic acid was formed, unless calcium carbonate was added. When a 10% glucose solution was introduced into flasks containing the fully grown fungus pad, rapid acid production began, especially when the pad was obtained in a medium containing calcium carbonate.

The following culture medium was at first employed

Glucose	100 g.
NH_4NO_3	2.0 g.
K_2HPO_4	1.0 g.
$MgSO_4 \cdot 7H_2O$	0.5 g.
$FeCl_3$	0.02 g.
Tap water	1000 cc.

In order to illustrate the balance of carbon and nitrogen in the growth of the organism, the results of a typical experiment are reported here. Three hundred-cc. portions of the medium were placed in 1000-cc. Erlenmeyer flasks,

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[1] Journal Series Paper of the Department of Soil Microbiology, N. J. Agr. Expt. Station.

[2] K. Saito, *Centrbl. Bakt.*, II, **29**, 289–290 (1911).

[3] E. Kanel, *Microbiologia*, **3**, 259–265 (1934).

[4] G. E. Ward, L. B. Lockwood, O. E. May and H. T. Herrick, THIS JOURNAL, **58**, 1286–1288 (1936).

[5] K. Miyaji, "Res. Bull. 10, Gifu Imp. Coll. Agr.," 1930.

[6] F. Ehrlich, *Ber.*, **52**, 63 (1919).

[7] T. Takahashi and T. Asai, *Centrbl. Bakt.*, II, **89**, 81–84 (1936).

sterilized by means of flowing steam, on three consecutive days, inoculated with the spores of the fungus, and incubated at 28°. After forty-eight hours of undisturbed growth, 5-g. portions of sterile calcium carbonate were added to the flasks. Some of these were shaken daily by hand, for one or two minutes, and some were left undisturbed. Analyses were made after five and nine days.

The results (Table I) show that *Rhizopus* consumed the ammonium ion in preference to the nitrate ion, and that the above medium contained a considerable excess of nitrogen above the nutrient requirements. The cell synthesis was not very extensive, since only about 13% of the glucose consumed was utilized to cover this requirement.[8] The preference of the organism for the ammonium ion is also brought out in another experiment. Three media were prepared containing glucose, minerals and calcium carbonate in the above proportions. Different forms of nitrogen were used, namely, ammonium sulfate, 5 g. per liter, ammonium nitrate, 2.5 g. and ammonium phosphate 2.5 g. per liter. The cultures were incubated for ten and seventeen days at 28° (Table II). All the three salts were utilized readily as sources of nitrogen, the sulfate being somewhat more efficient than the others.

TABLE I

GLUCOSE DECOMPOSITION BY *Rhizopus* MX

On basis of 1 liter of medium[a]

Incubation, days	Culture shaken	Glucose, g. Left	Glucose, g. Consumed	Nitrogen left, mg. NH_3–N	Nitrogen left, mg. NO_3–N	Dry weight of pellicle, g.	Nitrogen, in pellicle, mg.
5	+	19.1	65.1	75.0	310	8.45	217.3
5	−	28.0	56.2	110.0	330	6.96	208.0
9	+	..	..	..	...	9.74[b]	310.0

[a] Control contained 84.2 g. of pure glucose. [b] Ash in pellicle, 11.6%.

TABLE II

INFLUENCE OF NITROGEN SOURCE UPON ACID PRODUCTION BY *Rhizopus*

Nitrogen source	Incubation, days	*Rhizopus*	Glucose consumed, g.	Acid produced, g.[a]	Pellicle Dry weight, g.	Pellicle N, %
$(NH_4)_2SO_4$	10	No. 36	46.2	26.1	...	..
$(NH_4)_2SO_4$	10	MX	39.7	18.3	...	..
$(NH_4)_2SO_4$	17	No. 36	83.3	53.7	6.1	3.04
$(NH_4)_2SO_4$	17	MX	83.5	46.7	8.9	3.23
NH_4NO_3	10	No. 36	36.2	11.2	...	..
NH_4NO_3	10	MX	40.7	16.8	...	..
NH_4NO_3	17	No. 36	70.0	25.8	6.3	4.41
NH_4NO_3	17	MX	80.3	37.1	7.7	3.48
$(NH_4)_2HPO_4$	17	No. 36	62.4	29.9	...	..
$(NH_4)_2HPO_4$	17	MX	71.1	33.6	...	..

[a] Calculated from calcium equivalent.

In order to bring about the proper neutralization of the acid, it was sufficient to shake the flasks once or twice daily, for two or three minutes by hand, so as to bring the calcium carbonate, which was usually added in excess, in intimate contact with the acid. The results presented in Table III show that proper stirring of the culture, after a pellicle has been formed, which usually required forty-eight hours, is essential for maximum acid production.

TABLE III

INFLUENCE OF SHAKING UPON GLUCOSE DECOMPOSITION BY *Rhizopus* MX[a]

Treatment of culture	Glucose, g. Left	Glucose, g. Decomposed	Acid, produced, g.	Pellicle Dry weight, g.	Pellicle Ash, %	Pellicle Nitrogen, %
Unshaken	28.6	55.6	20.0	4.45	9.2	3.16
Shaken	10.9	73.3	30.9	..	...	..

[a] Thirteen days' incubation.

The medium was now modified, by reducing the concentration of the ammonium sulfate to 1.25 g. and the dipotassium phosphate to 0.5 g. per liter. The results of an experiment on prolonged incubation show (Table IV) that the most efficient production of the acid took place in eighteen days, at which time over 60% of the glucose was converted into acid; after twenty-eight days, the conversion was only 43%. When the acid was recovered by crystallization and alcohol precipitation, it was found to increase in calcium content with the age of the culture; the calcium oxide content of the younger cultures was 27.5% or close to the theoretical requirement for lactic acid, while in the older cultures it increased to 33 and even 35%. These results tend to confirm those of other investigators concerning the gradual transformation, in the older cultures of *Rhizopus*, of some of the lactic acid into lower acids.

TABLE IV

INFLUENCE OF PROLONGED INCUBATION ON ACID PRODUCTION BY *Rhizopus* FROM GLUCOSE

Organism	Incubation, days	Glucose consumed, g.	Acid produced, g.
MX	18	50.5	31.9
MX	25	75.2	..
MX	28	81.4	34.8
No. 36	18	36.8	22.3
No. 36	25	58.5	..

A large quantity of the calcium salt of the acid was now collected by concentrating the medium, crystallizing, dissolving the salt in hot water and reprecipitating with alcohol. The calcium salt was then acidified with phosphoric acid, extracted with ether and the zinc salt prepared. Both salts gave, by chemical analysis and rotation, the dextrorotatory form of the lactic acid.

When starch was substituted for glucose as a source of energy, active lactic acid production was also found to take place. Potato starch was used in the form of a paste, 50 g. per liter. The raw starch contained 86% of pure starch, by chemical analysis. Ammonium sulfate, as a source of nitrogen, and the above minerals were added to the medium. Five hundred-cc. portions were placed in 1000-cc. flasks and sterilized in flowing steam. The flasks were inoculated and incubated in an undisturbed condition for forty-eight hours at 28°; an excess of calcium carbonate was then added; the flasks were shaken twice daily. After seventeen days' incubation, the starch completely disappeared and 26.4 g. of lactic acid, calculated from the calcium salt, was produced per liter of medium. This is equivalent to a yield of over 60%.

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(8) On the basis of carbon content, this would be equivalent to over 15%.

The results of two other experiments, using culture MX, show (Table V) that the starch is at first transformed into reducing sugar, and the latter is gradually changed to lactic acid. The yield of the acid was as high with starch as a source of energy as with glucose, namely, 74.2% in the first experiment, and 50% in the second. Considerable sugar was left in the cultures in the last experiment, even after fourteen days.

TABLE V

PRODUCTION OF ACID BY *Rhizopus* FROM STARCH

On basis of 50 g. of raw potato starch[a]

Experiment 1			Experiment 2		
Period of incubation, days	Sugar as glucose, g.	Acid produced, g.	Period of incubation, days	Sugar as glucose, g.	Acid produced, g.
4	19.3	9.0	5[b]	23.2	8.4
6[b]	10.8	21.5	9	14.5	17.1
8	1.8	27.6	14	6.5	21.3
11	0.6	31.9			

[a] Equivalent to 43 g. of dry starch. [b] Starch completely disappeared.

A more detailed study was now made of the utilization of starch as a source of carbon for the production of lactic acid (Table VI). In the absence of calcium carbonate, no lactic acid accumulated; a large part of the starch was converted, however, into sugar, and remained as such; the growth of the organism was considerably less, and some of the starch remained unhydrolyzed even after eleven days. In the presence of calcium carbonate (1 g. per 2 g. of starch), the starch was also converted to sugar, but the latter was transformed rapidly to lactic acid. Nearly 60% of the starch was changed to the acid within eight days of incubation, and over 65%, in eleven days. After that period, the acid was gradually destroyed and became transformed to lower acids as shown by the increasing ash content. The nature of these acids was not determined.

TABLE VI

TRANSFORMATION OF STARCH TO SUGAR AND TO LACTIC ACID BY *Rhizopus*

On basis of 50 g. of raw potato starch[a]

	No $CaCO_3$		$CaCO_3$ present		
Incubation, days	Sugar as glucose, g.	Acid produced, g.	Sugar as glucose, g.	Acid produced, g.	CaO content of solution, g.
4	0.67	Trace	0.75	5.22	1.80
6	13.80	Trace	14.18	22.20	7.66
8	14.28	0	3.21	25.57	9.22
11	14.40	0	0	28.08	10.20
18	...	...	0	16.50	7.54

[a] Equivalent to 43 g. of dry starch.

A study of the influence of temperature on the lactic acid production revealed the fact that 28–37° was the optimum, the rate of the process being reduced rapidly above and below that temperature. A decrease in lactic acid production was accompanied, in starch media, to a certain point, by an increase in sugar accumulation, emphasizing the fact that two distinct enzyme mechanisms are responsible for the two processes.

Inulin was also utilized as a source of carbon by the organism, at a much slower rate, however, than either glucose or starch. Raw artichoke juice or cooked artichoke extract were used as sources of this carbohydrate. When the inulin was first hydrolyzed by means of a dilute mineral acid, lactic acid production took place more rapidly. No sugar accumulated in the inulin medium. These facts point to limited formation of the enzyme inulase by species of *Rhizopus*.

Summary

Two species of *Rhizopus*, isolated from composts of decomposing organic matter and from soil, were found capable of producing lactic acid from glucose, starch and inulin. As much as 60 to 70% of the first two carbohydrates was converted to the *d*-lactic acid in ten to eighteen days at 28°.

The starch was at first converted to sugar, and the latter gradually changed to lactic acid. When conditions were not favorable to the formation of the acid, as a lack of neutralizing agent or at an unfavorable temperature, the sugar accumulated.

Inulin was only slowly converted to lactic acid, due to insufficient production of inulase by the organisms.

NEW BRUNSWICK, N. J.

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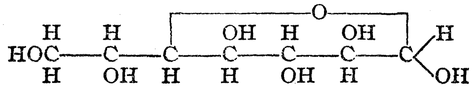
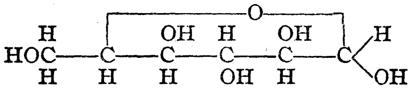
d-Beta-Galaheptose and Some of its Derivatives[1]

BY RAYMOND M. HANN AND C. S. HUDSON

In a recent publication[2] experimental details of the preparation and properties of *d*-alpha-galaheptose and of some of its derivatives were recorded. Attention was called to the close similarity of the configuration of this newly crystallized sugar to that of *l*-mannose, and the resulting similarity of the physical and chemical properties of these related sugars and of their compounds. In the present communication the properties of the epimeric *d*-beta-galaheptose, configurationally related to *l*-glucose, and of some of its derivatives, will be described.



α-Form of *d*-β-galaheptose (−19°)



β-Form of *l*-glucose (−19°)

This heptose was obtained in crystalline condition by Fischer,[3] but only cursory study of its behavior has been recorded. The sugar has an initial rotation[3a] of about −19° and mutarotates to an equilibrium value of −54°, comparable in magnitude with the recorded value for *d*-glucose, +19° (β-form) to +52°, and opposite in sign because the heptose is configurationally related to *l*-glucose, though it belongs in the *d*-series by Fischer's nomenclature. We name the heptose form of rotation −19° the alpha modification because its rotation is more toward the positive than the equilibrium rotation of the sugar (−54°), in accordance with generally accepted conventions; thus α-*d*-β-galaheptose and β-*l*-glucose are configurationally similar. This correspondence in rotation extends to several pairs of glucose and β-galaheptose derivatives and is sufficient for supplying an indication, though not a proof, of the structures and configurations in the β-galaheptose series. Because of the paucity of data in the *l*-glucose series the comparisons will refer to substances in the *d*-glucose series, which are opposite in sign of rotation.

TABLE I

COMPARISON OF SPECIFIC ROTATIONS [$[\alpha]^{20}\text{D}$] OF SUBSTANCES IN THE GLUCOSE AND β-GALAHEPTOSE SERIES

		d-Glucose series		*d*-β-Galaheptose series
Sugar (initial)	(β)	+ 19	(α)	−19
(final)		+ 52		−54
Aldonic acid phenylhydrazide		+ 12[4]		− 7.8
Aldonic acid amide		+ 31[5]		−20
Methyl glycoside	(β)	− 34.2[6]	(α)	+36
Ethyl mercaptal		− 29.8[7]		+37.8[8]
Benzyl mercaptal		− 98.4[9]		+73.8
Hexose pentaacetate	(α)	+101.6	(β)	−55.8
or				
Heptose hexaacetate	(β)	+ 3.8	(α)	+30.2
Methyl glycoside acetate	(β)	− 18.3	(α)	+51.8
Ethyl mercaptal acetate		+ 11.3[10]		+26.6[8]
Benzyl mercaptal acetate		+ 28.4[11]		+ 9.1

The parallelism noted in these rotations is evident also in the chemical behavior of the structurally related pairs of derivatives. Thus, *d*-glucose upon acetylation with sodium acetate and acetic anhydride yields largely the β-form of glucose pentaacetate which may be rearranged readily to the α-acetate by acid acetylating catalysts (zinc chloride or sulfuric acid). The heptose under the same conditions of acetylation yields a configurationally similar hexaacetate, which, because of conventions of nomenclature, is to be named the α-form, it being the more dextrorotatory member of a pair of isomers in the *d*-series. This acetate under the same experimental rearranging conditions yields the β-form, a result which may be anticipated due to the similarity in structure of the parent sugars. By application of the Koenigs and Knorr synthesis to β-*d*-glucose pentaacetate one obtains tetraacetyl-β-methyl glucoside while the same procedure with α-*d*-(β-galaheptose) hexaacetate yields pentaacetyl-α-methyl-*d*-β-galaheptoside. These results are

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Hann, Merrill and Hudson, THIS JOURNAL, **57**, 2100 (1935).

(3) Fischer, *Ann.*, **288**, 154 (1895).

(3a) Throughout the article the rotations are specific rotations at 20° for sodium light, unless otherwise stated.

(4) Hudson and Komatsu, THIS JOURNAL, **41**, 1141 (1919).

(5) Glattfeld and Macmillan, *ibid.*, **56**, 2482 (1934).

(6) Riiber, *Ber.*, **57**, 1797 (1924).

(7) Fischer, *ibid.*, **27**, 673 (1894).

(8) Hann and Hudson, THIS JOURNAL, **56**, 2080 (1934).

(9) Pacsu, *Ber.*, **57**, 849 (1924).

(10) Wolfrom, THIS JOURNAL, **51**, 2190 (1929).

(11) Unpublished results.

in complete agreement with those obtained in earlier studies in the mannose and α-galaheptose series and support the hypothesis that the physical and chemical properties of the heptose sugars may be in first measure predicted from the space configurations of carbons one to five inclusive, which show that aldohexose to which the heptose is similar.

The isorotation rules allow the calculation of the expected values of the rotations of some of these compounds; Table II summarizes these data.

TABLE II

OBSERVED AND CALCULATED SPECIFIC ROTATIONS $[\alpha]^{20}\mathrm{D}$ IN THE *d*-β-GALAHEPTOSE SERIES

Substance	Obsd.	Calcd.
Sugar (α-form)	−19°	− 10°
(β-form)	. .	− 91°
α-Methyl glycoside	+36°	. . .
α-Methyl glycoside acetate	+52°	. . .
β-Methyl glycoside	. .	−131°
β-Methyl glycoside acetate	. .	− 72°
α-Acetate	+30°	+ 35°
β-Acetate	−56°	− 54°

From well-known considerations of isorotation, the molecular rotation (30,830) of α-methylglucoside may be written as $A_{\mathrm{CH}_3} + B$, where A_{CH_3} is the contribution of the aldehydic carbon atom and B that of the basal chain, to the total rotation. The same considerations allow the expression $-A_{\mathrm{CH}_3} + B$ to signify the molecular rotation (−6630) of β-methylglucoside. By subtracting these equations one can evaluate the quantity A_{CH_3} as +18,730.[12] From α- and β-glucose, similarly, a value of A_{OH} of +8460 is obtained. Upon the assumption that A_{CH_3} will not differ widely in value in configurationally similar sugars, the molecular rotation of α-methyl-*d*-β-galaheptoside (8060) may be expressed as $18{,}730 + B' = 8060$, whence B' in the galaheptose series becomes −10,670 and the calculated molecular rotation of the α-form of *d*-β-galaheptose becomes $A_{\mathrm{OH}} + B' = -2210$, corresponding to a specific rotation of about −10°. The unknown β-form would be $-A_{\mathrm{OH}} + B'$, or −19,130 in molecular rotation and −91° in specific rotation. The calculated molecular rotation of the unknown β-methyl-*d*-β-galaheptoside is $-A_{\mathrm{CH}_3} + B'$, −29,400, corresponding to −131° in specific rotation.

By introducing the value of A'_{CH_3} (26,950) derived from the acetylated methyl glucosides[12] into the equation expressing the molecular rotation of pentaacetyl-α-methyl-*d*-galaheptoside, $A'_{\mathrm{CH}_3} + B_{\mathrm{Ac}} = +22{,}600$, one obtains the value of B_{Ac} in the β-galaheptose series as −4350 and this substituted in the expression $-A'_{\mathrm{CH}_3} + B_{\mathrm{Ac}}$ yields a molecular rotation of −31,300, indicating that the now unknown pentaacetyl-β-methyl-*d*-β-galaheptoside will have a specific rotation near −72°. Similar considerations using the value of A_{Ac} (20,700) of the glucose series and B_{Ac} (−4350) give calculated values of +35 and −54° for the specific rotations of α- and β-*d*-β-galaheptose hexaacetate, respectively, in good agreement with the observed values of +30 and −56°.

In the preparation of β-galaheptonic amide use was made of the excellent method of Glattfeld and Macmillan;[5] sirupy β-galaheptonic lactone when dissolved in liquid ammonia readily yielded the desired crystalline amide. This substance rotated in the levo direction in accordance with the amide rule. The previously described phenylhydrazide also shows a negative rotation as would be expected from the phenylhydrazide rule. The mercaptals in pyridine agree in sign of rotation with those of the *l*-glucose series, but their acetates, measured in chloroform, do not; evidently no generalization regarding rotation may now be made of these open chain mercaptal derivatives.

Experimental

d-(β-Galaheptonic) Phenylhydrazide from d-Galactose.—Hydrocyanic acid was added to 500 g. of *d*-galactose as described previously.[2] The filtrate from the separation of the α-galaheptonic amide was transferred to a 3-liter Erlenmeyer flask and boiled with 400 g. of barium hydroxide octahydrate until ammonia was no longer evolved (twelve to fifteen hours), the volume being maintained at about 1500 cc. by occasional addition of water. The barium was precipitated by addition of 385 to 400 cc. of 6 *N* sulfuric acid, the barium sulfate was removed and the solution was balanced until free of sulfate and barium ions. It was adjusted to a volume of 1500 cc., 140 cc. of phenylhydrazine and 40 cc. of acetic acid were added and the solution was heated for five hours on the steam-bath. After cooling, the phenylhydrazide of α-galaheptonic acid was removed (fraction I), the filtrate was concentrated to 750 cc. and an equal volume of 95% alcohol was added. The next day the separated solid was filtered off (fraction II), the filtrate concentrated to 500 cc., an equal volume of alcohol added and after standing overnight the third fraction was removed. The filtrate was concentrated to 200 cc. and 200 cc. of 95% alcohol was added to obtain the final fraction. From seven preparations the average yields and specific rotations of the fractions were as follows:

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(12) Dale and Hudson, THIS JOURNAL, **52**, 2535 (1930).

fraction I, 133 g., +8.00°; fraction II, 96 g., −7.21°; fraction III, 12.5 g., +7.35°; fraction IV, 30.2 g., −5.80°.

Pure β-galaheptonic phenylhydrazide of specific rotation −7.8° and melting at 189–190° (corr.) was obtained by combining fractions II and IV, dissolving in 15 parts of water and allowing the solution to stand for twenty-four hours at 20° when the major portion of the α-phenylhydrazide separates. The β-isomer was recovered by concentrating the solution to one-half its volume and adding an equal volume of 95% alcohol. Fischer reports a melting point of 185° (uncorr.) and a specific rotation of −6.32°. Kiliani[13] reports 185° (uncorr.).

***d*-(β-Galaheptonic) Amide from *d*-(β-Galaheptonic) Phenylhydrazide.**—A solution of 100 g. of pure phenylhydrazide and 80 g. of copper sulfate pentahydrate in 1000 cc. of water was refluxed for five hours and filtered from the separated solid. The solution, freed of copper by hydrogen sulfide, was treated with a warm solution of 500 g. of barium hydroxide octahydrate in 500 cc. of water, the barium sulfate was filtered off and the filtrate was balanced until free of barium and sulfate ions. The yield of β-galaheptonic acid, as shown by titration, was 65.8 g. (92%). A portion of the galaheptonic acid sirup, which had been lactonized in part by heating for twenty-four hours on the steam-bath, upon standing for several weeks dried to a hard vitreous non-crystalline solid. A solution of 5.9 g. of this material in 150 cc. of liquid ammonia was allowed to evaporate to a sirup spontaneously at room temperature, then transferred to a vacuum desiccator over sulfuric acid and the residual ammonia removed, crystallization occurring during the process. The dark brown solid was dissolved in 20 cc. of water, 40 cc. of 95% alcohol added and the solution decolorized by carboraffin. Upon seeding, the amide crystallized in a yield of 3 g. It was recrystallized to constant properties by solution in one part of warm water and addition of one part of 95% alcohol, separating in colorless needles, melting at 170–171° (corr.) and having a specific rotation of −20° in water. (0.1940 g. in 25 cc. in a 4-dm. tube rotated 0.62° to the left.)

Anal. Calcd. for $C_7H_{15}O_7N$: N, 6.2. Found: N, 6.2.

***α-d*-(β-Galaheptose).**—The acid solution from 100 g. of pure *d*-(β-galaheptonic) phenylhydrazide was concentrated *in vacuo* to a thin sirup, transferred to a 3-liter beaker and heated on the steam-bath for eighteen hours. The heavy sirup was dissolved in 200 cc. of cold water and reduced in the usual manner with 2000 g. of 2.5% sodium amalgam. Following removal of the sodium sulfate by alcohol, the reduced solution was concentrated to a thin sirup which became a crystalline magma after several days. The crystals were separated by thinning the magma with a small amount of 50% alcohol, filtering and drying. The average yield of 13 experiments was 23.2 g. (38% based on the acid concentration). The sugar was recrystallized conveniently by solution in 2 parts of warm water and addition of 10 parts of warm 95% alcohol, separating in prisms, melting at 196–197° (corr.) with decomposition, and showing an equilibrium specific rotation in water of −54°. Fischer reports the corrected melting point as 195–199° and the rotation at equilibrium as −54.4°. The course of its mutarotation is recorded in Table III. It is designated the alpha form of *d*-(β-galaheptose) because the course of mutarotation indicates it to be the less levorotatory form of a sugar of the *d*-series. The mutarotation follows the unimolecular formula and the extrapolated initial rotation is about −19°.

TABLE III

MUTAROTATION OF α-*d*-[β-GALAHEPTOSE] IN WATER

Concentration 1.0027 g. in 25 cc. solution: tube length 2 dm.; $T = 20 \pm 0.5°$.

Time after making solution, min.	$[\alpha]^{20}_D$	Time min.	$k_1 + k_2$
5	−20.72	0	...
15	22.01	10	0.0017
30	24.60	25	.0022
75	30.86	70	.0023
90	32.80	85	.0023
105	34.96	100	.0024
120	36.25	115	.0024
135	37.55	130	.0024
150	38.84	145	.0024
165	40.14	160	.0024
180	41.43	175	.0024
195	42.73	190	.0025
210	43.80	205	.0025
225	44.45	220	.0025
240	45.32	235	.0025
270	46.61	265	.0025
330	48.98	325	.0025
345	49.20	340	.0025
375	49.85	370	.0025
12 hrs.	53.95 (equilibrium)		...
48 hrs. (final)	53.95	...	...
		Average	.0024

***α-d*-(β-Galaheptose) Hexaacetate.**—A suspension of 20.4 g. of oven-dried β-galaheptose and 5 g. of fused sodium acetate in 80 cc. of redistilled acetic anhydride was heated gently to incipient reaction, when the heat of reaction was sufficient to bring about a rise in temperature to the boiling point of the anhydride. Following subsidence of the reaction the solution was refluxed for fifteen minutes, cooled and poured into crushed ice, the crystalline acetate separating as the excess anhydride decomposed; yield 36 g. (80%). α-*d*-(β-Galaheptose) hexaacetate crystallizes from 10 parts of methyl alcohol in groups of colorless needles, 5 to 6 mm. long, giving the appearance of a silky mat upon filtration. The substance melts at 151–152° (corr.) to a clear colorless oil and when recrystallized to constant specific rotation gives a value of +30.2° (0.5002 g. in 25 cc. of chloroform in a 2-dm. tube rotated 1.21° to the right).

Anal. Acetyl: 0.2179 g. consumed 28.4 cc. of 0.1 *N* NaOH. Calcd. for six acetyl groups, 28.3 cc. Calcd. for $C_{19}H_{26}O_{13}$: C, 49.33; H, 5.67. Found: C, 49.34; H, 5.68.

***β-d*-(β-Galaheptose) Hexaacetate.**—A solution of 5.0 g. of α-*d*-β-galaheptose hexaacetate in 25 cc. of a rearranging solution, prepared by adding 2.3 cc. of concd. sulfuric acid dropwise to an ice-cold mixture of 68 cc. of acetic anhydride and 29 cc. of glacial acetic acid, showed a progressive change in specific rotation from +18.7 to −68.9° in forty-eight hours at 20°. The solution was poured upon cracked ice and the gum which separated was crystallized by repeated trituration with cold water; yield 3.3 g.

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(13) Kiliani, *Ber.*, **55**, 99 (1922).

(66%). *β*-*d*-(*β*-Galaheptose) hexaacetate crystallizes from 5 parts of 50% ethyl alcohol in small needles melting at 100–101° (corr.) and when recrystallized to constant specific rotation showed a value of −55.8° (0.5150 g. in 25 cc. of chloroform in a 2-dm. tube rotated 2.3° to the left).

Anal. Calcd. for $C_{19}H_{26}O_{13}$: C, 49.33; H, 5.67. Found: C, 49.25; H, 5.68.

α - Methyl - *d* - (*β* - Galaheptoside) Pentaacetate.—A solution of 10 g. of *α*-*d*-(*β*-galaheptose) hexaacetate in 50 cc. of acetic acid saturated with gaseous hydrobromic acid was allowed to stand for one hour, concentrated *in vacuo* (bath 40°) to remove the major part of the acid and twice treated with 100 cc. of toluene and concentrated to a sirup, to remove the residual acid. The dry sirup was dissolved in 100 cc. of methyl alcohol and 10 g. of silver carbonate was added. Following completion of the reaction, which proceeded with local generation of heat, the hot solution was filtered to remove silver halide, the glycoside acetate crystallizing from the filtrate as it cooled; yield 6.9 g. (73%). *α*-Methyl-*β*-galaheptoside pentaacetate crystallizes from 5 parts of 50% acetic acid in colorless elongated plates, melting at 122–123° (corr.) and exhibits a specific rotation of +51.8° in chloroform (0.5717 g. in 25 cc. in a 2-dm. tube rotated 2.37° to the right), these properties remaining unchanged upon recrystallization.

Anal. Calcd. for $C_{18}H_{26}O_{12}$: C, 49.74; H, 6.04; OCH_3, 7.1. Found: C, 49.56; H, 6.02; OCH_3, 7.1.

α - Methyl - *d* - (*β* - Galaheptoside).—A solution of 4.8 g. of pentaacetyl-*α*-methyl-*d*-*β*-galaheptoside in 25 cc. of methyl alcohol was saturated with gaseous ammonia, allowed to stand overnight and concentrated *in vacuo* to dryness, crystallization occurring during the process. The dry solid was taken up in methyl alcohol, the solution filtered through carboraffin, and upon cooling the filtrate yielded the glycoside in a yield of 2.0 g. (80%). *α*-Methyl-*d*-*β*-galaheptoside crystallizes from methyl alcohol in small clear prisms, melting at 182–183° (corr.) without decomposition. Its specific rotation in water when pure is +36.0° (0.4096 g. in 25 cc. in a 2-dm. tube rotates 1.18° to the right).

Anal. Calcd. for $C_8H_{16}O_7$: C, 42.83; H, 7.20; OCH_3, 13.8. Found: C, 42.95; H, 7.28; OCH_3, 13.8.

***d*-(*β*-Galaheptose) Benzyl Mercaptal.**—A solution of 5 g. of powdered *d*-*β*-galaheptose in 10 cc. of concentrated hydrochloric acid was shaken with 10 cc. of benzyl mercaptan, crystallization occurring at the end of one and one-half hours. After a further half hour, 50 cc. of ice water and 25 cc. of 95% alcohol were added and the mercaptal filtered off; yield 3.3 g. (31%). The mercaptal crystallizes from 10 parts of 95% alcohol in a cottony mass of minute needles, which melt at 146–147° (corr.) and give a specific rotation of +73.8° in pyridine (0.2303 g. in 10 cc. in a 1-dm. tube rotated 1.70° to the right).

Anal. Calcd. for $C_{21}H_{28}O_6S_2$: S, 14.56. Found: S, 14.51.

Hexaacetyl-*d*-(*β*-galaheptose) Benzyl Mercaptal.—To a solution of 2.6 g. of *d*-*β*-galaheptose benzyl mercaptal in 20 cc. of pyridine, 20 cc. of acetic anhydride was added and the reaction mixture allowed to stand overnight. Upon pouring the solution into crushed ice and stirring, crystallization readily took place; yield 4.1 g. (quantitative). The mercaptal acetate was purified by recrystallization from 5 parts of 95% alcohol, separating in well formed prisms. The substance, recrystallized to constant physical properties, melts at 82–83° (corr.) and gives a specific rotation of +9.2° (0.3047 g. in 10 cc. of chloroform in a 1-dm. tube rotated 0.28° to the right).

Anal. Calcd. for $C_{33}H_{40}O_{12}S_2$: S, 9.26. Found: S, 9.10.

Summary

A number of crystalline derivatives of *d*-(*β*-galaheptose) have been prepared and described. Attention has been called to the parallelism in rotational behavior of certain derivatives of *d*-*β*-galaheptose with those of the configurationally related *l*-glucose. This similarity extends also to the chemical behavior of these sugars and would indicate that such properties are conditioned by the spacial arrangement of carbons one to five in the sugar molecule.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE LANKENAU HOSPITAL RESEARCH INSTITUTE]

Permonosulfuric Acid in Organic Media*

BY GERRIT TOENNIES

Permonosulfuric acid as an oxidizing agent in organic synthetical work has been employed almost exclusively in the form of aqueous solutions.[1] It is the purpose of this paper to record some data on the behavior of permonosulfuric acid in various alcohols and in a nitrile.

Permonosulfuric Acid, Preparation and Analytical.—The peracid was prepared either from potassium persulfate and sulfuric acid (method A)[2a] or from hydrogen peroxide[2b] and chlorosulfonic acid (method B).[3] Permonosulfuric acid was determined iodometrically by thiosulfate (about 0.025 *N*) titration. When the excess of iodide is kept small (about 0.005 *M*), the first end-point obtained on *rapid* titration, *immediately* after adding the peracid to a solution containing starch, potassium iodide and, if necessary (for securing an excess of acid over the iodide consumed), some sulfuric acid, corresponds to permonosulfuric acid (as established by comparison with the more generally specific method of Müller and Holder[4]). The accuracy of the initial reading can be improved by subtracting a correction equal to the small additional amount of iodine liberated on waiting again as long as was required to reach the first end-point. A subsequent end-point obtained after addition of molybdate yields the sum of permonosulfuric acid and hydrogen peroxide as long as persulfuric acid ($H_2S_2O_8$) is present in minor amounts. The total peroxygen was determined according to Lubarski and Dikowa.[5] Free acidity, including one acid group of H_2SO_5,[6] is obtained at the methyl red end-point, while five to ten minutes of boiling with excess (about 0.01 *N*) sodium hydroxide was found necessary[7] for the determination of total acidity ($H_2SO_5 \longrightarrow H_2SO_4 + O$, $H_2S_2O_8 + H_2O \longrightarrow 2H_2SO_4 + O$). In the concentrated peracid solutions prepared according to method B (*vide infra*) water was calculated by the difference between the sum of the directly determined constituents and the total.

Permonosulfuric Acid in Organic Media. General.—The relative stability of permonosulfuric acid solutions in 75% methanol has been mentioned.[8] Solutions containing about 10% water were made with 92% ethanol, and others of 3 to 5% water content, with isopropyl alcohol (98–99%, "petrohol"), isoamyl alcohol (Merck Reagent) and acetonitrile (Merck Reagent). Reaction mixtures obtained by method A[9] were stirred by portions into the solvent, which was kept below −15° by addition of solid carbon dioxide. In the case of isoamyl alcohol it was found preferable to grind the alcohol (of −15°) in portions into the almost solid reaction mass contained in a mortar imbedded in freezing mixture (thus dispensing with the need for carbon dioxide). In the cases of the lower alcohols or acetonitrile the insoluble salt is filtered by suction, while an amyl alcohol solution is better separated by centrifuging. Other solutions, of low $H_2SO_4{:}H_2SO_5$ ratios, were made by carefully adding concentrated peracid, prepared according to method B, to alcohol of less than −10° (*vide infra* on explosions).

Yields.—Table I gives a summary of the solutions prepared on the basis of method A. The fact (not shown in the table) that the total peroxygen recovery, *i. e.*, including the amount found in the solid residue, was 96–100% of that contained in the starting material, indicates that the yield of permonosulfuric acid in solution is limited by incompleteness of the reaction between sulfuric acid and persulfate and by incomplete separation from the solid residue (in order to maintain the concentration of the filtrate as high as possible no washings were added) rather than by loss of oxygen. Variations in the time the sulfuric acid–persulfate reaction mixture was allowed to stand (one to eighteen hours at 0° or two hours at room temperature) showed no definite effect on the yield. The solid residue appears to be chiefly $KHSO_4 + H_2O$ and additional H_2SO_4, approaching $2KHSO_4 + H_2SO_4$ in the case of isoamyl alcohol. In the ethanol experiment the washed and dried (at 125°) residue weighed 128 g. which, calculated as $KHSO_4 + H_2O$ (acid equivalent found 149, calculated 154), is equal to 98.5% of the potassium used. Three preparations according to method B, from 140, 160 and 250 mml. of chlorosulfonic acid and the equivalent amounts of hydrogen peroxide (85, 81 and 91%, respectively[2b]), gave permonosulfuric acid yields of 77 ± 1%. The resulting oily solutions (they did not crystallize at −15°) contained per gram, 6.2 ± 0.3 mml. of H_2SO_5, 1.9 ± 0.1 mml. of H_2SO_4, 0.8 ± 0.3 mml. of H_2O_2, 3.4 ± 0.6 mml. of H_2O, 0.0–0.2 mml. of $H_2S_2O_8$ and less than 0.02 mml. of Cl_2. These solutions keep well at low temperatures. At −12° the determined molarities of H_2SO_5 and H_2O_2 had changed from 6.01 and 0.80 to 6.19 and 0.65 after fourteen days and to 6.09 and 0.57 after fifty-nine days. However, care must be exercised in handling since contact with such organic matter as textiles, wood, paper causes immediate ignition.

(*) Aided by a grant for Fundamental Research from E. R. Squibb & Sons.

(1) *Cf.* Houben, "Methoden der organischen Chemie," Vol. 2, third ed., p. 222, 1925. The only exceptions were found in a paper published in 1900 by Baeyer and Villiger [*Ber.*, **33**, 860, 862 (1900)] who used dilutions of their "dry Caro reagent" in acetic acid and in ethanol.

(2) (a) Baeyer and Villiger, *ibid.*, **32**, 2628 (1899); Gleu, *Z. anorg. allgem. Chem.*, **195**, 70 (1931), and others; (b) obtained according to Hurd and Puterbaugh, THIS JOURNAL, **52**, 950 (1930).

(3) D'Ans and Friedrich, *Z. anorg. Chem.*, **73**, 345 (1912).

(4) Müller and Holder, *Z. anal. Chem.*, **84**, 410 (1931).

(5) Lubarski and Dikowa, *ibid.*, **81**, 450 (1930).

(6) *Cf.* H. Ährle, *Z. angew. Chem.*, **22**, 1713 (1909).

(7) Th. S. Price [*J. Chem. Soc.*, **89**, 53 (1906)] noted that on the acid side, even at boiling temperature, the complete acid value is slow to be reached.

(8) G. Toennies, THIS JOURNAL, **56**, 2198 (1934).

(9) *Cf.* footnote 2a. The chief difficulty in maintaining low temperature and achieving intimate mixing of the components—both essential—appears at a stage when an appreciable part of the persulfate has been added and when rather suddenly the reaction spreads through the mixture as evidenced by rising temperature and stiffening of the whole mass. Previous reports do not appear to have mentioned this phenomenon.

TABLE I

PERMONOSULFURIC ACID SOLUTIONS. SUMMARY OF PREPARATIONS

No.	$K_2S_2O_8$ mml. used	Molar ratio $\frac{H_2SO_4{}^a}{K_2S_2O_8}$ used	Solvent used	Yield in soln., % of peroxygen used H_2SO_5	Total per-O	Concn. in soln. Free acid, normal. (N_A)	H_2SO_5, molarity (M_0)	Acid in residue, % of total potential acid[b]
1	420	4.65	500 cc. ethanol	75	78	5.8	0.60	20
2	410	4.65	500 cc. isopropanol	53	55	6.4	.51	32
3	37	4.65	50 cc. isoamyl alcohol	54	66	5.1	.51	40
4–7	100–230	3.00	Isoamyl alcohol[c]	41 ± 4	51 ± 5	4.4 ± 0.2	.53 ± 0.05	47 ± 4
8	370	4.65	450 cc. acetonitrile	44	52	5.9	.31	16

[a] The sulfuric acid used was of 92.5% concentration in preparations 1–7, and of 96% in number 8. [b] *I. e.*, including that from $K_2S_2O_8 + H_2O \longrightarrow K_2SO_4 + O + H_2SO_4$. [c] The amount used was equal in cc. to the mml. $K_2S_2O_8$ used, *e. g.*, 230 cc. for 230 mml. of $K_2S_2O_8$.

Stability and Reactions. (a) **in Alcohols.**—In order to obtain some initial information on the factors of stability of, and the nature of the reactions involved in, alcoholic solutions of the peracid, the ethanol solution described above and two ethanolic dilutions, one of one-half and one of one-quarter the original concentration, were each divided into three portions, and of these one was kept at room temperature (about 26°), one in a refrigerator (about 2°) and one in the low temperature compartment of the refrigerator (about −12°). On each of these nine portions periodical determinations were made of permonosulfuric acid, total peroxygen, free acidity and total acidity. The results are given in Fig. 1. A comparison of plots 1, 2 and 3 indicates that the rate of decomposition of permonosulfuric acid is higher in presence of higher acid concentration. Since in none of the solutions formation of free oxygen ($2H_2SO_5 \longrightarrow 2H_2SO_4 + O_2$, $H_2SO_5 + H_2O_2 \longrightarrow H_2SO_4 + H_2O + O_2$ or $2H_2O_2 \longrightarrow H_2O + O_2$)—the cause of decreasing strength in pure aqueous solutions—was perceptible, and since the characteristic odor of ethyl acetate became very noticeable as the peracid disappeared from the alcoholic solutions, the decrease in total peroxygen may be attributed to formation of acetic acid which in the presence of the prevailing high concentrations of acid and

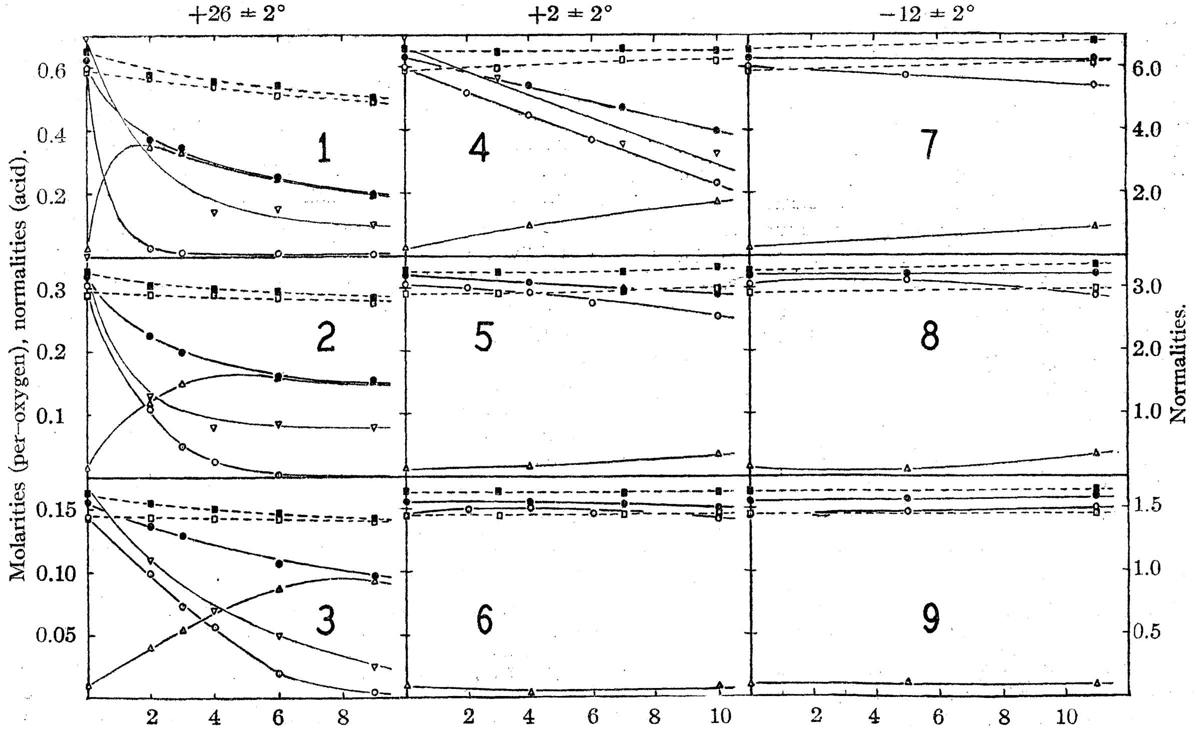

Fig. 1.—The behavior of ethanolic solutions of permonosulfuric acid. Full lines refer to the left ordinate scale, broken lines to the right ordinate scale. "Molarity (peroxygen)" is used to signify number of g.-atoms of active oxygen per 1000 cc. ■, total acid; □, free acid; ▽, acid formed by alkaline boiling (total minus free acid); ●, total peroxygen; ○, permonosulfuric acid; △, peroxygen other than H_2SO_5 ("non-SO_5," *i. e.*, total peroxygen minus permonosulfuric acid). The plots of the nine individual experiments are numbered 1 to 9.

alcohol would be expected to esterify to a large extent. On account of attending difficulties[10] quantitative determination of the ester was not attempted in this exploratory work. Assuming that the reaction $H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$ is substantially irreversible as it is in aqueous solution[11] the "non-SO_5 peroxygen" would consist of one or several of the possible neutral peroxides (hydrogen peroxide, mono- or diethyl peroxide). The oxidation to acetic acid (as measured by the decrease in total peroxygen) is effected by permonosulfuric acid as well as by the "non-SO_5" fraction (although at a lower rate by the latter) as evidenced in plots 1, 2 and 3 by the continued decrease in total peroxygen after the permonosulfuric acid has become nearly zero. The decrease in total acidity which is evident at room temperature is presumably due to formation of ethylsulfuric acid, which is highly resistant to alkaline hydrolysis (Beilstein), while an increase in free acidity, visible in plot 4, may be attributed to hydrolysis of residual persulfuric acid. The main practical result expressed in Fig. 1 is the observation that at about −10° temperatures are approached at which all other reactions become negligible compared with the transfer of oxygen atoms from H_2SO_5 to "non-SO_5" combinations, while even the speed of this reaction drops below one per cent. per day.

Results quite similar to those shown for the ethanol solution were obtained with regard to the stability of the isopropyl alcohol solution (Table I). The concentrated solution showed at −12°, over a period of nine days, a decrease in permonosulfuric acid of 1.1% per day, while all other changes were negligible. In an isopropyl alcohol dilution to one-quarter the original strength the corresponding rate of decrease was 0.5% per day. The stability of the peracid in similar isoamyl alcohol solutions was somewhat less; solutions nos. 4–7 (Table I) showed rates of decrease of 2.5–3.9% per day. However, the effect of acidity on the stability is also marked here. Table II shows results obtained on a solution made by adding 4.7 cc. of a concentrated permonosulfuric acid solution, prepared according to method B, to isoamyl alcohol of −12° and making up to 100 cc. The average rate of decrease of the peracid is about 0.8% per day, while the sum of $H_2SO_5 + H_2O_2$ decreased only by 4.7% over the whole ninety day period, indicating that the main reaction occurring is a shift of oxygen between permonosulfuric acid and hydrogen peroxide.

TABLE II

STABILITY OF PERMONOSULFURIC ACID IN ISOAMYL ALCOHOL at −12°

Days	−4[a]	0	5	13	34	90
H_2SO_5, M	0.502	0.534	0.514	0.482	0.397	0.258
H_2O_2, M	.102	.042	.060	.087	.166	.291
H_2SO_4, M	.167	.116				
H_2O, M	.243					

[a] This column shows the values calculated from the analytical data and the weighed amount used, of the concentrated H_2SO_5 solution which was made and analyzed four days prior to the amyl alcoholic solution.

(b) **In Acetonitrile.**—In the acetonitrile preparation (solution no. 8, Table I) the total recovery of the peroxygen used (including that contained in the solid residue) was 98%. The stability of the resulting solution is apparent from the data of Table III. In contrast to the rapid decomposition at room temperature[12] the solution is of useful stability at −13°.

TABLE III

STABILITY OF PERMONOSULFURIC ACID IN ACETONITRILE

Days	t	H_2SO_5 M_0	Total per-O M_0	Free acid N_A	Total acid N_A
0	30 ± 2°	0.317	0.378	5.88	6.30
0.25[a]		.014			
1[b]		.009	.229	5.34	6.44
2[c]		.004	.224	4.93	6.32
10[d]		.000	.185		
0	−13 ± 2°	.317	.378	5.88	6.30
2		.326			
4		.328		5.83	6.20
10			.330		
44		.19			
70		.13			

[a] Due to heat of reaction temperature of flask has risen to about 40°. [b] Orange color and odor of acetic acid present. [c] Also odor of sulfur dioxide present. [d] On further standing gradually a heavy brown oil settles out, leaving a colorless supernatant liquid of pure acetonitrile odor.

(c) **Explosions.**—In studying the effect of the medium it became desirable to use at least one secondary and one tertiary alcohol for comparison with the primary ones. An advantage expected from these alcohols was slower esterification with sulfuric acid and concomitantly slower formation of water the presence of which is undesirable for some purposes. The alcohols chosen were *s*-methylisobutylcarbinol (Eastman, practical) and *t*-ethyldimethylcarbinol (Eastman).[13] Especially with regard to the tertiary one there was the additional expectation of greater resistance against oxidation by permonosulfuric acid, based on determinations of oxidation velocities by alkaline permanganate, of Tronov, Lukanin and Pavlinov[14] who for the tertiary amyl alcohol reported a velocity constant of about $^1/_{500}$ of that of isoamyl alcohol, while they found the oxidation velocity of secondary alcohols generally a little higher than that of the primary ones. Addition of concentrated peracid (made by method B) to 9.5 cc. of 1.1 M H_2SO_4 (using 99% H_2SO_4) in methylisobutylcarbinol at −10°, to make a 0.50 M H_2SO_5 solution, was done without difficulty, while in the corresponding operation using ethyl-

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(10) Indications were obtained that the acid which is liberated by alkaline boiling and which results from decomposition of H_2SO_5 and $H_2S_2O_8$ as well as from saponification of ethyl acetate, may be further increased by oxidation of alcohol to acid, occurring during the alkaline boiling.

(11) Palme, *Z. anorg. allgem. Chem.*, **112**, 47 (1920).

(12) It seems probable that the rapid decomposition is linked to the acid catalyzed hydrolysis of acetonitrile [*cf.* Lavine and Toennies, *J. Biol. Chem.*, **101**, 727 (1933)].

(13) Their relative speeds of esterification were determined by measuring the change in acidity at room temperature of small samples containing anhydrous sulfuric acid at a concentration of approximately twice molar. After four days the free acidity of the solution of the primary alcohol had diminished 32%, that of the secondary 15%, while that of the tertiary was substantially unchanged, although after three days an initial drop of about 5% had taken place. We can suggest no reason for this subsequent increase in free acidity.

(14) Tronov, Lukanin and Pavlinov, *J. Russ. Phys.-Chem. Soc.* **59**, 1173 (1927); *cf. C. A.*, **22**, 3336 (1928).

dimethylcarbinol an explosive reaction occurred on addition of few drops of the concentrated peracid, in spite of careful cooling. After thorough purification—by twice allowing to stand overnight with an excess of concentrated permanganate solution, washing, drying with barium oxide and fractionating (collected between 101.6° and 102.5°)—this tertiary alcohol still showed the same explosive tendencies, indicating that impurities can hardly be considered responsible for this behavior. A more dramatic demonstration of potential dangers occurred when a repetition, with fourfold amounts, of the above methylisobutylcarbinol experiment resulted in a violent detonation. Local overheating leading to a cumulative reaction evidently represents a real danger, at least in this particular alcohol. The following experiments throw some additional light on the danger factors. 0.30 cc. of concentrated peracid (11.7 M H_2SO_5, 3.3 M H_2SO_4, 0.6 M H_2O_2, 5.3 M H_2O) was added to 4 cc. of each of the following, cooled in freezing mixture: (a) isoamyl alcohol, (b) 4 M H_2SO_4 (99.4%) in isoamyl alcohol, (c) methylisobutylcarbinol, (d) 4 M H_2SO_4 in methylisobutylcarbinol. Of the resulting solutions (c) exploded after about one minute and (d) a little later, both while remaining in the freezing mixture. (a) and (b) were taken to room temperature after fifteen minutes, and now (a) exploded after several minutes while (b) did not explode. Obviously the primary $C_5H_{11}OH$ is less reactive than the secondary $C_6H_{13}OH$ and the latter in turn is more stable than the tertiary $C_5H_{11}OH$. The apparent reduction of explosibility by the presence of considerable sulfuric acid (about 37.5%) may be caused by the dilution of the organic component. It should be noted that the permonosulfuric acid concentration used (about 0.8 M) as well as the sulfuric acid concentration are considerably higher than those encountered in the solutions described in the earlier part of this paper, and in which no explosive tendencies were ever observed, even though considerable quantities were handled.

The writer wishes to express his appreciation of the assistance rendered by Dr. Mary A. Bennett in some phases of the experimental work.

Summary

Methods for obtaining solutions of permonosulfuric acid in some of the lower alcohols, including isoamyl alcohol, and in acetonitrile have been described. Examples illustrating the nature of the slow decompositions taking place in such solutions have been given and it has been shown that at −12° solutions containing as much as 0.6 M H_2SO_5 are of convenient stability. Attention is called to the possibility of explosive reactions with secondary and tertiary alcohols, and generally in cases of too high concentrations of the peracid.

PHILADELPHIA, PENNA. RECEIVED NOVEMBER 12, 1936

[CONTRIBUTION FROM THE LANKENAU HOSPITAL RESEARCH INSTITUTE]

A New Method for the Preparation of Permonophosphoric Acid[1]

BY GERRIT TOENNIES

Permonophosphoric acid since its discovery in 1910 by Schmidlin and Massini[2] has received little attention although it is distinguished by a remarkable oxidizing power (lower manganese salts are oxidized, in the cold, to permanganate). The method of Schmidlin and Massini, consisting in gradually combining phosphoric anhydride and concentrated hydrogen peroxide in very small portions, is difficult on account of the violence of the interaction, and uncertain as to result in spite of its tediousness. The only other method proposed by Fichter and associates,[3] produces by anodic oxidation mixtures of alkali salts of H_3PO_5 and $H_4P_2O_8$ in solutions of potassium fluoride and therefore is of limited usefulness. The present experiments were undertaken with a view of simplifying the production of this interesting compound by moderating the reaction between phosphoric anhydride and hydrogen peroxide through the use of suitable inert diluents for the latter.

Of three solvents studied, ether, isoamyl alcohol and acetonitrile, only the last one gave satisfactory results. Acetonitrile is completely inert against phosphoric anhydride and it can be used to make solutions of hydrogen peroxide of high concentration and high stability.[4] In two parallel experiments, in which the components were used in ratios approximately corresponding to the assumed reaction

$$P_2O_5 + 2H_2O_2 + H_2O \longrightarrow 2H_3PO_5 \qquad (I)$$

phosphoric anhydride (5.55 and 5.18 mml., respectively,) was suspended in 1.5 cc. of acetonitrile (Merck reagent) and at low temperature (freezing mixture) an acetonitrile solution (1.10 and 1.05 cc.) containing hydrogen peroxide[5] (12.94 and 12.35 mml.) and water (4.03 and 3.84 mml.) was added slowly. Besides, 0.30 cc. of acetonitrile was

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(1) Aided by a grant for fundamental research from E. R. Squibb and Sons.

(2) Schmidlin and Massini, *Ber.*, **43**, 1162 (1910).

(3) Fichter and associates, *Helv. Chim. Acta*, **1**, 297 (1918); **2**, 3 (1919); S. Husain and J. R. Partington, *Trans. Faraday Soc.*, **24**, 235 (1928).

(4) G. Toennies and M. Elliott, results to be published shortly in THIS JOURNAL.

(5) Hydrogen peroxide of 80 to 90% concentration was prepared according to Hurd and Puterbaugh, THIS JOURNAL, **52**, 950 (1930).

added in the first case, and 0.30 cc. of acetonitrile containing 0.023 mml. of 2,4-dinitrobenzenesulfonic acid[6] in the other case. The purpose of this modification was to examine the possibility that the reaction between phosphoric anhydride and hydrogen peroxide might be catalyzed by strong acids, as it has been found that the reaction between aliphatic anhydrides and hydrogen peroxide in non-aqueous systems is highly susceptible to acid catalysis.[4] The phosphoric anhydride was in both instances energetically attacked and cooling was necessary for some time to keep the reaction mixture from exceeding room temperature. Some escape of gas was visible and the odor of ozone appeared, to which after a while the characteristic "peracid" odor (known from perbenzoic and permonosulfuric acid) was added. Analysis—by the methods previously (*cf.* preceding paper) used by the author for solutions of permonosulfuric acid—after twenty hours gave for the two solutions, respectively: peracid 56 and 57%, hydrogen peroxide 20 and 18.5%, total peroxygen 76.5 and 76.5%, all in terms of the hydrogen peroxide used. In terms of phosphoric anhydride the result is that 65.3 and 68.0%, respectively, have been converted into permonophosphoric acid. The agreement between the two experiments, surprisingly close for a heterogeneous reaction of this character, indicates the absence of acid catalysis as a rate determining factor, and the data further show that the desired reaction takes place to a satisfactory extent in acetonitrile and that no peroxide other than permonophosphoric acid, such as perphosphoric acid $H_4P_2O_8$,[2,3] is formed. It should be stated here that the conclusion that the peroxide (previously referred to as "peracid") formed is permonophosphoric acid, is based on the following considerations: (1) the evidence of Schmidlin and Massini[2] indicating that the compound resulting from interaction of phosphoric anhydride and hydrogen peroxide is permonophosphoric acid, (2) observations[4] that solutions of hydrogen peroxide in acetonitrile are extremely stable and show no evidence of formation of a peroxide which reacts rapidly with iodide in the manner observed here and which is indistinguishable from the analogous action of permonosulfuric acid, (3) acidimetric evidence (described in connection with the next experiment, *vide infra*) that the acid left after removal of the peroxygen is H_3PO_4 and not HPO_3 which should result if the peracid present had the formula HPO_4, and (4) the qualitative observation that these acetonitrile solutions cause oxidation of Mn^{++} to MnO_4^- in the cold, a reaction which, according to the discoverers,[2] distinguishes permonophosphoric acid from other peroxides.

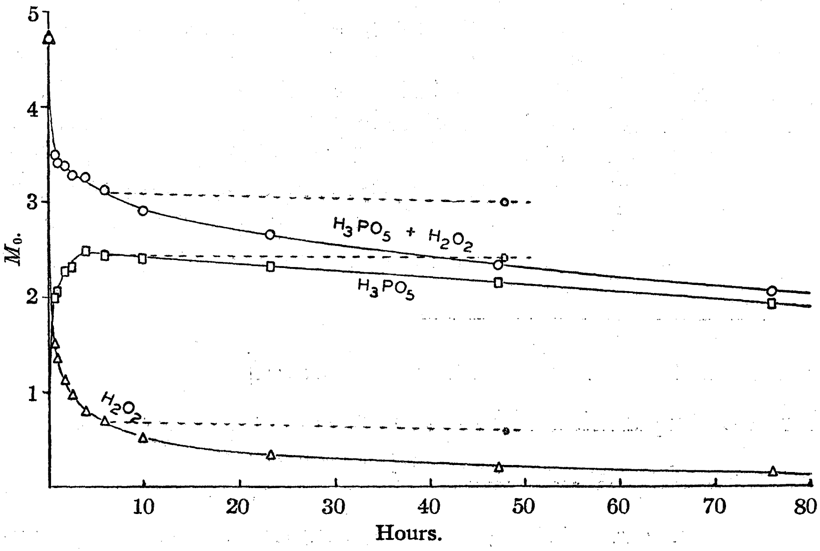

Fig. 1.—The reaction between phosphoric anhydride and hydrogen peroxide at room temperature (about 25°). M_0 indicates molarity in peroxygen, *e. g.*, 1 M H_3PO_5 or 1 M H_2O_2 = 1 M_0. The moment when the hydrogen peroxide was completely added has been taken as zero time. The dotted lines show the stabilizing effect of low temperature, obtained by keeping a part of the solution at about −12°.

The next experiment was designed to throw some light on the rate of formation of the peracid. To a suspension of 15.55 mml. of phosphoric anhydride in 4 cc. of acetonitrile, cooled in freezing mixture, 3.05 cc. of an acetonitrile solution containing 35.87 mml. of hydrogen peroxide and 11.34 mml. of water were added slowly during about five minutes. After three additional minutes the mixture was brought to room temperature and after forty-five minutes of standing, with occasional shaking, very little phosphoric anhydride remained undissolved. From this point on, 0.1-cc. samples were withdrawn periodically (by means of a Folin micro blood sugar pipet; the average deviation in the size of the sample obtained was ±0.15%) and analyzed. The data obtained are plotted in Fig. 1. They show that the bulk of the peracid is formed within the first hour, during the dissolving of phosphoric anhydride, that most of the loss of peroxide occurs during this period, and that even after the phosphoric anhydride has completely dissolved (about 100 minutes) additional peracid is formed. The yield of peracid at the maximum (four hours) is 60.5% in terms of phosphoric anhydride. Further work is planned to study the mechanism of the reaction and the factors influencing it. To determine if metaphosphoric acid, or its hypothetical per-derivative (HPO_4) might be present in the solution, acidimetric titrations were carried out as follows: about two hours after the beginning of the reaction 0.1-cc. samples were added to 0.8 cc. of 0.6 M dibenzyl sulfide in acetonitrile. This causes the transfer of the active peroxygen to dibenzyl sulfide, thus eliminating it as a disturbing factor in acidimetry since the resulting dibenzyl sulfoxide is relatively inert as an oxidizing agent. Titration with 0.05 N NaOH to the turning point of (a) methyl orange (pH 4) and (b) thymolphthalein (pH 10) gave the following results: (a) 4.07, 4.16 N, (b) 8.36, 8.58 N. The 1:1 ratio is in agreement with H_3PO_4 (and possibly

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[6] *Cf.* G. Toennies and M. Elliott, This Journal, **57**, 2136 (1935).

$H_4P_2O_7$) and suggests absence of appreciable amounts of a monobasic acid (HPO_3).

The relative stability at room temperature of this peracid in acetonitrile is remarkable in comparison with that of solutions of permonosulfuric acid in acetonitrile (*cf.* preceding paper). Since the peroxygen of H_3PO_5 is more active than that of H_2SO_5 it appears likely that the difference in stability is due to catalytic effects of the accompanying acids, inasmuch as H_3PO_4 is a weak acid compared with H_2SO_4. Just as permonosulfuric acid (*cf.* preceding paper), so also permonophosphoric acid can be kept in isoamyl alcoholic solution, the stability being of a similar order. Dilutions of the first two acetonitrile solutions described here with 10 volumes of isoamyl alcohol showed, in terms of the yields reported above, after three days at $-11°$, the presence of 51 and 50.5% (instead of initially 56 and 57%) of peracid and of 71.5% of peroxygen (instead of 76.5%) in both cases.

When instead of acetonitrile, ether or isoamyl alcohol was used as the medium for the interaction between hydrogen peroxide and phosphoric anhydride, the results were as follows. An ether solution, about 2.8 *M* in hydrogen peroxide and 0.85 *M* in water, left in contact, for twenty-four hours at room temperature, with an amount of phosphoric anhydride corresponding to the hypothetical reaction

$$P_2O_5 + H_2O_2 \longrightarrow HPO_3 + HPO_4 \qquad \text{(II)}$$

showed little action upon the solid phase. Analysis of the whole reaction mixture showed 2.5% of the hydrogen peroxide as such, 17% as peracid and a total peroxygen recovery of 26%. When the components were used in ratios corresponding to reaction (I) (2.5 *M* H_2O_2, 1.2 *M* H_2O) the phosphoric anhydride went into solution within two hours, forming an oily layer. Analysis showed a total recovery of 9.4% as peracid and 68% as hydrogen peroxide. After twenty hours the corresponding figures were 14 and 44% showing that formation of additional peracid proceeds much slower than loss of hydrogen peroxide. In similar experiments using isoamyl alcohol as the medium less than 2% of the hydrogen peroxide was converted into peracid.

Summary

A convenient method for the preparation of solutions of permonophosphoric acid, based on the heterogeneous interaction between phosphoric anhydride and hydrogen peroxide in acetonitrile, has been described and it has been shown that such solutions, even at room temperature, are relatively stable. When instead of acetonitrile, ether or isoamyl alcohol is used as the medium, the reaction between hydrogen peroxide and phosphoric anhydride is of negligible extent.

PHILADELPHIA, PENNA. RECEIVED NOVEMBER 12, 1936

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

A Comparison of Hydrogen, Quinhydrone and Glass Electrodes in Magnesium Sulfate Solutions

BY E. S. AMIS AND J. L. GABBARD

The error of the glass electrode compared with that of the hydrogen electrode in solutions of various ions has received much attention,[1-8] and the rapid increase in its use in various *p*H studies and industrial processes justifies further investigation. Therefore, the authors have made a direct comparison of the hydrogen, quinhydrone and glass electrodes in buffered and unbuffered, except for small quantities of hydrochloric acid, magnesium sulfate solutions.

Apparatus and Materials

The glass electrodes having a resistance of the order of 10^7 ohms were blown of Corning 015 glass in the form of a thin bulb[1,9] on the end of a tube of ordinary soft glass and aged for at least twenty-four hours before using. The silver–silver chloride electrode of the reduced oxide type[10] was placed in the 0.1 *N* hydrochloric acid inside the glass electrode and served as the reference electrode. The hydrogen electrodes were made in the usual manner and the quinhydrone electrodes were made and cleaned as recommended by Morgan, Lammert and Campbell.[11] The hydrogen electrodes were also cleaned in this manner before being platinized. This cleaning process was repeated and the hydrogen electrodes were newly platinized before each series of measurements. The platinum black was removed from the hydrogen electrodes by the use of hot aqua regia. Two hydrogen and two quinhydrone electrodes were used in making the measurements. If the difference in potential between the two respective electrodes was not less than 0.2 mv., a new pair of electrodes was selected. The calomel electrode was prepared from the Leeds and Northrup chemicals especially purified for the purpose. Commercial tank hydrogen was purified as described by Dole.[4] Since

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(1) W. S. Hughes, *J. Chem. Soc.*, 491 (1928).

(2) F. Quittner, *Ann. Physik*, [4] **35**, 745 (1928).

(3) D. A. MacInnes and D. Belcher, THIS JOURNAL, **53**, 3315 (1931).

(4) M. Dole, *ibid.*, **53**, 4260 (1931).

(5) M. Dole, *ibid.*, **54**, 3095 (1932).

(6) M. Dole, *J. Phys. Chem.*, **36**, 1570 (1932).

(7) M. R. Thompson, *Bur. Standards J. Research*, **9**, 833 (1932).

(8) G. Buchbock, *Z. physik. Chem.*, **A156**, 232 (1931).

(9) G. R. Robertson, *Ind. Eng. Chem., Anal. Ed.*, **3**, 5 (1931).

(10) G. Jones and M. Hartmann, THIS JOURNAL, **37**, 752 (1915).

(11) J. L. R. Morgan, O. M. Lammert and M. A. Campbell, *ibid.*, **53**, 454 (1931).

only comparative results were being sought, the solutions were made of commercial C. P. salts without further purification by accurately weighing the salts on an analytical balance, dissolving and diluting in a calibrated flask. The weaker solutions were made by diluting the stronger ones. The buffered solutions were made according to the directions given by Clark,[12] and standardized with the hydrogen electrodes. The quinhydrone was prepared by the Eastman Kodak Company.

The electrode vessel for the buffered solutions was similar to that used by Hovorka and Dearing,[13] consisting of four cylindrical separatory funnels of 80-ml. capacity sealed together and holding, respectively, the hydrogen, the glass and the quinhydrone electrodes and the connecting arm of the calomel electrode. The vessel for the unbuffered solutions was a 250-ml. Pyrex beaker containing the glass and the quinhydrone electrodes and the connecting arm of the calomel electrode.

The circuit used in the construction of the vacuum tube potentiometer was that described by DuBridge and Brown[14] modified to measure small potentials and to meet other requirements. The sensitivity of the potentiometer was 0.05 mv. and since there was no perceptible drift during the time required to make a measurement and neither body capacity nor external electrostatic fields had any effect upon its operation, the measurements could be repeated easily with a precision of 0.2 mv.

Experimental Procedure

The experiments consist of a direct comparison of the glass, hydrogen and quinhydrone electrodes in buffered magnesium sulfate solutions of various concentrations and slightly differing *p*H values, and also a comparison of glass and quinhydrone electrodes in unbuffered, except for very small quantities of dilute hydrochloric acid, magnesium sulfate solutions of various concentrations but of constant *p*H values. However, in the latter, different series at different *p*H values were studied, providing a means of observing the effect upon the electrode potentials caused by changing both the concentration and the *p*H values of the solutions.

With the glass, hydrogen, calomel and quinhydrone electrodes immersed in the same solutions connected by stopcocks as in the case of the buffered solutions, the following cells could be formulated

(A) Hydrogen–Quinhydrone Pt, H_2/soln., H^+ (a), Quinhydrone/Au

(B) Hydrogen–Glass Pt, H_2/soln./glass/0.1 *N* HCl/AgCl/Ag

(C) Glass–Quinhydrone Ag/AgCl/0.1 *N* HCl/glass/soln., H^+ (a), Quinhydrone/Au

(D) Hydrogen–Calomel Pt, H_2/soln.//sat. KCl/HgCl/Hg

(E) Calomel–Quinhydrone Hg/HgCl/sat. KCl//soln., H^+ (a), Quinhydrone/Au

(F) Glass–Calomel Ag/AgCl/0.1 *N* HCl/glass/soln.//sat. KCl/HgCl/Hg

The values for all these cells were obtained where possible for each solution and the values of D, E and F used to check the direct readings of A, B and C. The procedure followed in the actual measurement of the cells in the buffered solutions was similar to that used by Hovorka and Dearing,[13] with the exception that in this work the vacuum tube potentiometer was used for measuring all potentials. The quinhydrone electrodes were very unstable in the solutions of *p*H 7 or above.

In the solutions where a constant *p*H based on the readings of the quinhydrone electrodes was maintained, the quinhydrone electrodes were allowed to come to equilibrium in the unbuffered solutions and the e. m. f. of cell E noted. Then dilute (0.0101 *N*) hydrochloric acid was added dropwise, with stirring after each addition, until the e. m. f. corresponding to the desired *p*H was obtained, the glass electrodes were placed in the solution and the readings made. The hydrogen electrodes were unstable in these solutions, particularly those of higher *p*H values.

Results and Discussion

It is noted by observing cells A, B and C that as long as the quinhydrone and glass electrodes act as perfect hydrogen electrodes the values of the respective cells will remain constant and independent of the *p*H of the solutions. The potential of cell A is

$$(1)\quad E = E_h + E_q = -RT/F \ln aH^+ + E_0 - RT/2F \ln ah/aq + RT/F \ln aH^+$$

$$(2)\quad = E_0 - RT/2F \ln ah/aq$$

where ah, aq and aH^+ are the activities of the hydroquinone, quinone and hydrogen ions, respectively. E_0 is the normal potential of the quinhydrone electrode (0.69938 v. at 25°).[13] Since the presence of dissolved substances may cause the value of the second term of equation (2) to vary due to the alteration of the activity ratio of the hydroquinone to the quinone, it is expected that the constant value of cell A should be slightly different from 0.69938 v., the actual value depending upon the kind of salts present and their con-

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[12] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1927, p. 106.

[13] F. Hovorka and W. C. Dearing, THIS JOURNAL, **57**, 446 (1935).

[14] L. A. DuBridge and H. Brown, *Rev. Sci. Instruments*, **4**, 532 (1933).

TABLE I

DATA SHOWING THE QUINHYDRONE ELECTRODE ERROR (QE), THE GLASS ELECTRODE ERROR (GE) AND THE GLASS–QUINHYDRONE ERROR (GQ) IN MILLIVOLTS IN BUFFERED[a] MAGNESIUM SULFATE SOLUTIONS

		Temperature, 29°						Temperature, 25°	
		Cell A constant 0.6979 v.	Cell B constants		Cell C constants			Cell B constants	
M	*p*H	QE	Glass No. 1 0.3651 v. GE	Glass No. 2 0.3574 v. GE	Glass No. 1 0.3328 v. GQ	Glass No. 2 0.3405 v. GQ	*p*H	Glass No. 6[b] 0.3540 v. GE	Glass No. 9[b] 0.3543 v. GE
0.1	4.15	−0.2	0.0	−0.4	−0.2	0.2	7.71	0.1	0.2
.2	3.98	.3	− .1	.0	.4	.0			
.5	3.77	− .3	− .2	− .2	.0	− .2	7.42	− .3	− .1
1.0	3.44	− .1	.0	− .1	.1	.2	7.23	.1	− .1
2.0	3.01	1.0	−1.4	− .7	2.6	1.7	6.96	−1.1	−1.3

[a] The buffered solutions used in preparing the solutions of lower *p*H contained 0.05 *M* potassium acid phthalate and 0.004 *M* NaOH while the buffer used for the higher *p*H solutions contained 0.05 *M* H_3BO_3, 0.05 *M* KCl and 0.004 *M* NaOH. [b] The Dole–MacInnes type of glass electrode. *M* Molar concentration.

TABLE II

DATA SHOWING GLASS–QUINHYDRONE ERRORS (GQ) IN MAGNESIUM SULFATE SOLUTIONS OF DIFFERING *p*H VALUES

	*p*H 5.88 and 27° Constants			*p*H 5.21 and 27° Constants			*p*H 4.30 and 26° Constants	
M	Glass No. 5 0.3444 v. GQ	Glass No. 4 0.3461 v. GQ	*M*	Glass No. 3 0.3326 v. GQ	Glass No. 7 0.3355 v. GQ	*M*	Glass No. 5 0.3444 v. GQ	Glass No. 6 0.3395 v. GQ
1.87	8.9	9.3	2.09	9.8	9.9	2.05	4.7	5.1
1.25	5.4	5.8	1.53	6.5	6.6	1.53	3.4	3.8
0.63	1.4	1.6	1.04	3.7	3.9	1.02	2.4	2.2
.5	0.5	0.8	0.52	1.2	1.3	0.51	1.0	1.0
.25	.5	.7	.26	0.3	0.4	.25	0.1	0.1
			.21	.5	.6	.20	− .1	− .1
.13	.3	.3	.10	.2	.2	.10	.2	.2

centrations. However, as long as the value remains constant with change of magnesium sulfate concentration, it is evident that the *a*h/*a*q ratio is remaining constant and the quinhydrone electrode is functioning as a perfect hydrogen electrode.

The value of cell B has been discussed by Dole[4] (p. 4064). The value of cell C should be the value of cell A minus the value of cell B (0.6994 − 0.3524 = 0.3470 v. at 25°). Therefore, the constant value of this cell varies with each particular series of experiments. The constant values for cells A, B and C were obtained for each series of experiments by taking the values of the cells in the solutions of increasing concentration, plotting these values against the concentration, and extrapolating for the value of the cell at zero concentration. Any deviation of the cells from their constant values in each series of experiments is termed, respectively, the "quinhydrone electrode error," the "glass electrode error" and the "glass–quinhydrone error" and shown in Tables I and II. From Table I it is observed that neither the glass nor the quinhydrone electrodes show an appreciable error in 1 *M* concentration or less of buffered magnesium sulfate solutions below *p*H 4.15, but in the 2 *M* concentrations it is seen that each electrode has an appreciable error. The "glass–quinhydrone error" is, as would be expected, in close agreement with the numerical sum of the errors, disregarding sign, of the two electrodes.

The error of the glass electrode is negative, which means that the error is not a function of the positive magnesium ions. If the positive magnesium ions were entering or being adsorbed by the glass membrane of the glass electrode, it is easily seen by observing cell B that the error would be positive, in agreement with the observations of other investigators upon other positive ions.[3,4,6] If the equation (3) $\Delta E = S\,RT/F \ln a\mathrm{H_2O} = RT/F \ln \frac{p\,\mathrm{H_2O\ in\ MgSO_4}}{p\,\mathrm{H_2O}}$ derived by Dole[5] for the glass electrode functioning as a water electrode is used, letting $S = 1$, and using the vapor pressure of water and of water in magnesium sulfate solution at 50° as given in the "International Critical Tables," −1.2 mv. is obtained for the error in 2 *M* solution and −0.5 mv. in 1 *M* solution. The temperature interval of 21° (50 to 29°) would cause little change in the calculated error since Carpenter and Jette[15] have shown that the

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(15) C. D. Carpenter and E. R. Jette, THIS JOURNAL, **45**, 578 (1923).

p H_2O in $MgSO_4/p$ H_2O ratio for a saturated solution of magnesium sulfate is practically constant with change of temperature. In a trial calculation ΔE changed less than 0.2 mv. in going from 50 to 70° where the greatest change in the ratio as influenced by temperature is observed. Assuming that the concentration of the buffers in the solutions would have very little effect upon the total water vapor pressure, -1.2 mv. is in excellent agreement with the observed values except the value for the glass electrode No. 2. Therefore, it is felt that the observed error of the glass electrodes is due to the water error of the glass electrode.

The "quinhydrone error" is due to the "salt error"[13,16–18] of the quinhydrone electrode. From equation (2) it is seen that $E_s = -RT/2F \ln a\text{h}/a\text{q}$ where E_s is the "salt error" or the deviation of potential produced by the change of the activity coefficient ratio of the hydroquinone to quinone. Kiss and Urmanczy[18] showed that this error in salt concentrations above 1 N could be expressed by the linear relation (4) $E_s = C\mu + D$ where μ is the ionic strength of the solution and C and D are constants characteristic of the salt ($C = 0.300$ and $D = 1.3$ for magnesium sulfate). Hovorka and Dearing[13] have more recently shown that the error can be expressed by the more simple linear relation (5) $E_s = AN$ with A being a constant characteristic of the salt (0.00122 for magnesium sulfate) and N the normality of the solution. The data reported by these investigators were obtained by dissolving magnesium sulfate in 0.01 N hydrochloric acid. Table III contains a comparison of the data taken with the magnesium sulfate solutions at pH 4.30 in this investigation with theirs. When corrections are made for the water error of the glass electrodes in the higher concentrations it is seen that the data agree closely.

Table III

The "Salt Error" of the Quinhydrone Electrode in Magnesium Sulfate Solutions of Various Concentrations from Different Investigations

	Kiss and Urmanczy $MgSO_4$ in 0.01 N HCl		Hovorka and Dearing $MgSO_4$ in 0.01 N HCl		This investigation Pure $MgSO_4$ brought to pH 4.30 by use of dilute HCl Glass No. 5		Glass No. 6	
M	E_m, mv.	E_c, mv.	E_m, mv.	E_c, mv.	E_m, mv.	$E_{corr.}$	E_m, mv.	$E_{corr.}$
0.25	1.0	1.6	0.68	0.61	0.1		0.1	
.5	1.7	1.9	1.32	1.22	1.0		1.0	
1.0	2.4	2.5	2.40	2.44	2.4		2.2	
1.25	2.8	2.8						
1.5	3.1	3.1			3.4	2.6	3.8	3.0
2.0	4.0	3.7			4.7	3.5	5.1	3.9

E_m = measured errors; E_c = calculated errors and $E_{corr.}$ = corrected errors.

The data in Table II show that the "glass–quinhydrone errors" in the unbuffered solutions of higher pH, particularly in the higher concentrations, are much larger than in the solutions of lower pH. They are also much larger than those calculated by equations (4) and (5), even after corrections are made for the water error of the glass electrode. This is to be expected when it is considered that the pH of quinhydrone in pure water is about 5.85[19,20] which means that in the solutions of higher pH considerable ionization of the hydroquinone is taking place. This may affect the electrode potential as shown by La Mer and Parsons[21] by changing the electrode reaction from

$$C_6H_4O_2 + 2H^+ + 2e \rightleftharpoons C_6H_4(OH)_2 \text{ to } C_6H_4O_2 + 2e \rightleftharpoons C_6H_4O_2^{--}$$

or it may affect the actual pH of the solution by taking part in the acid base equilibrium by removing OH^- ions.

Kolthoff and Bosch[20] found close agreement between the quinhydrone and hydrogen electrodes in weakly buffered solutions ranging in pH from 3.6 to 7.2, which would indicate that the buffered solutions not only hold the activity coefficients of the hydrogen ion constant, but also tend to hold the ratio of the activity coefficients of the hydroquinone to the quinone constant thus preventing the "salt error." This would explain the absence of any appreciable "salt error" for the quinhydrone electrodes in the buffered solutions below one molar concentrations.

Acknowledgments.—To Dr. Malcolm Dole of the Department of Chemistry, Northwestern University, the authors wish to give sincere thanks for his many helpful suggestions during this investigation and for his constructive criticisms of the data. To Dr. F. E. Tuttle, Professor *Emeritus*, of the Chemistry Department, University of Kentucky, they wish to express their appreciation for interest and suggestions during this investigation and in the preparation of the manuscript.

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(16) S. P. L. Sørensen, M. Sørensen and K. Linderstrøm-Lang, *Ann. Chim.*, **16**, 283 (1921).

(17) A. Urmanczy, *Magyar Chem. Folyoirat*, **39**, 1925 (1933).

(18) A. V. Kiss and A. Urmanczy, *Z. physik. Chem.*, **A169**, 31 (1934).

(19) R. J. Best, *J. Phys. Chem.*, **34**, 1815 (1930).

(20) Kolthoff and Bosch, *Biochem. Z.*, **183**, 435 (1927).

(21) V. K. La Mer and T. R. Parsons, *J. Biol. Chem.*, **57**, 613 (1923).

Summary

1. It has been shown that the presence of magnesium ions to the extent of two moles per liter does not affect the potential of the glass electrode.

2. The water error of the glass electrode in magnesium sulfate solutions has been found to conform well with the equation $\Delta E = S\,RT/F \ln a'H_2O$ as derived by Dole.

3. It has been shown that the glass electrode is suitable for measuring the "salt error" of the quinhydrone electrode in solutions buffered with only traces of hydrochloric acid, and that this error depends upon the pH of the solution.

LEXINGTON, KY. RECEIVED NOVEMBER 25, 1936

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

The Entropy of Water from the Third Law of Thermodynamics. The Dissociation Pressure and Calorimetric Heat of the Reaction $Mg(OH)_2 = MgO + H_2O$. The Heat Capacities of $Mg(OH)_2$ and MgO from 20 to 300°K.

BY W. F. GIAUQUE AND R. C. ARCHIBALD

The thermodynamic properties of water are sufficiently important and interesting to invite the fullest possible investigation. The present work was undertaken because it had been shown[1] that the experimental $\int_0^T C_p \, d \ln T$ for water does not give the correct entropy. This quantity is accurately known from the band spectrum data.

It seemed desirable to perform at least one experiment in which the third law of thermodynamics would give the entropy of water accurately and in a straightforward manner. The reaction $Mg(OH)_2 = MgO + H_2O$ was selected for this purpose for several reasons. First, a measurable dissociation occurs at a rather low temperature, although not at as low a temperature as we were led to expect from the erroneous available data. Second, the identity of the water molecule should be very completely lost in magnesium hydroxide and such difficulties as are present in ice, or conceivably in water of crystallization, should not be present. Third, the reaction is one which is well adapted to an accurate calorimetric investigation of the heat of reaction. Fourth, the atoms in the substances concerned are all of low atomic weight, which makes the measured and extrapolated quantities of entropy low, with a corresponding increase in the accuracy of the entropy of water derived from the experimental data.

The entropy of water was obtained from the thermodynamic relation

$$S_T(H_2O) = S_T(Mg(OH)_2) - S_T(MgO) + (\Delta H_T/T) + R \ln P_T \quad (1)$$

where ΔH_T and P_T are the heat and pressure of dissociation, respectively, at temperature T. It safely may be assumed that the fugacity is equal to the pressure at the low pressures and high temperatures of the experiment. We may state at once that complete agreement was found between the entropy value obtained as above and that derived from the molecular spectrum of water.

Since this research was undertaken the heat capacity of ice has been reinvestigated accurately by Giauque and Stout.[2] They have shown that the entropy discrepancy is in very exact agreement with the quantitative predictions of Pauling,[3] who bases his calculation on false equilibrium at low temperatures with respect to the random orientation of hydrogen bonds in ice.

More recently Long and Kemp[4] have made similar measurements on deuterium oxide. They have shown that a similar discrepancy exists in this case and find that it also is in quantitative agreement with the calculated discrepancy of Pauling.[3]

While there is no reason to doubt the reliability of the entropy of water as deduced from the accurately known band spectrum, and although this value is strongly supported by the above investigations, we believe that it is very desirable to have one or more third law checks on this important quantity.

Preparation and Purity of Magnesium Hydroxide and Magnesium Oxide.—Crystalline magnesium hydroxide was prepared by the method of de Shulten.[5] A wide-mouthed platinum bottle of one liter capacity was used. This fitted closely inside a well-insulated vertical tubular

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[1] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

[2] Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

[3] Pauling, *ibid.*, **57**, 2680 (1935).

[4] Long and Kemp, *ibid.*, **58**, 1829 (1936).

[5] De Schulten, *Compt. rend.*, **101**, 72 (1885).

electric oven. A typical charge for the bottle was: 1375 g. of potassium hydroxide, 48.5 g. of $MgCl_2 \cdot 6H_2O$ and 243 cc. of water. The charge was heated in the oven to 210°C. and held at this temperature until the solution became clear. This required about thirty minutes from the time heating was started. It was then allowed to cool to room temperature in the oven. This required about eighteen hours. The solid mass was dissolved out of the platinum bottle with water and filtered through a sintered glass filter. The crystals of magnesium hydroxide remaining on the filter were washed several times with distilled water. When a sufficient quantity of the crystals had been made they were given a final washing with water and dried for two hours in an oven at 100°C.

The crystals were well formed and of an average diameter of about 0.2 mm. A photograph of a representative sample of the crystals is shown in Fig. 1.

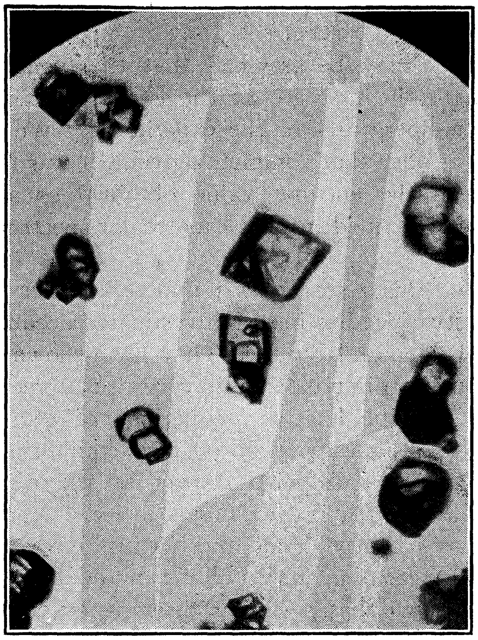

Fig. 1.—Photograph of representative sample of magnesium hydroxide crystals. The average diameter was about 0.2 millimeter.

Since the main impurities possible in the magnesium hydroxide are potassium and phosphate from the potassium hydroxide, analyses were made for these substances. These analyses gave potassium as K, 0.15%, and phosphate as PO_4, less than 0.005% of the magnesium hydroxide. The material was protected carefully from carbon dioxide and a test showed that carbonate was not present.

In order to obtain magnesium oxide as it exists in equilibrium with the magnesium hydroxide used, the hydroxide was decomposed under vacuum at 300°C., and the temperature raised to 350°C. toward the end of the decomposition. The decomposition was attempted at 200°C. but was very slow. At 300°, however, it was about 95% complete in ten days. All of the measurements on magnesium oxide were made with this material and the results corrected for the amount of magnesium hydroxide present. The small amount of potassium hydroxide impurity was assumed to have the same heat capacity as magnesium hydroxide. Such error as is involved by this assumption could hardly have an appreciable effect on the heat capacity results. The effect of impurity on the heat of solution measurements will be discussed in that connection.

The Heat Capacities of Magnesium Hydroxide and Oxide.—The heat capacities were measured in a manner and calorimeter similar to that described by Giauque and Wiebe,[6] but, the weight of the heavy, hollow, lead-copper, thermally isolated cylinder that served as an enclosure for the calorimeter was about 50% greater. The electrical leads were carried through the protective cylinder by insulated wire sealed in, for a length of about 7 cm., with a low melting alloy.

The calorimeter was of copper 10.8 cm. in length and 3.8 cm. in diameter and with twelve radial vanes. The gold resistance thermometer-heater was wound on the outside of the calorimeter and brought into good thermal contact by Bakelite lacquer. A short German silver tube, through which the calorimeter was filled, was attached to the bottom of the calorimeter. This tube was provided with a soldered cap containing a pin hole through which the air was pumped out and helium admitted, after which the hole was closed with solder. The helium was necessary to ensure good thermal conductivity. The German silver tube permitted soldering without appreciable heating of the calorimeter.

The resistance thermometer was calibrated by means of standard thermocouple No. 16[7] which was attached to the bottom of the calorimeter. A small correction to the original calibration was applied on the basis of a recent comparison with the oxygen and hydrogen vapor pressure thermometers and the melting point, 54.39°K., and higher transition point, 43.76°K., of oxygen.

The thermocouple was brought through the protective cylinder in a paraffin filled tube. The resistance thermometer, which gave high precision and accuracy over short intervals of temperature, was calibrated at about five-degree intervals over the entire range of investigation. The calibrating was done concurrently with the heat capacity measurements.

All low temperatures were produced by means of liquid air or liquid hydrogen, transferred from laboratory supply dewars. In calculating energy, 1.0004 absolute joules were taken equal to 1 international joule and 4.185 absolute joules were taken equal to 1 calorie.

The heat capacity data are summarized in Tables I and II and are shown graphically in Figs. 2 and 3. 173.203 g. of magnesium hydroxide and 118.671 g. of magnesium oxide were used in the measurements.

In Table III the data have been presented in the form of values taken from smooth curves through the experimental values. Since the equilibrium measurements had to be extended to higher temperatures than had been indicated by the erroneous available data a considerable extrapolation was necessary in the case of mag-

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[6] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

[7] (a) Giauque, Buffington and Schulze, *ibid.*, **49**, 2343 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

TABLE I

MOLAL HEAT CAPACITY OF MAGNESIUM OXIDE

Molecular weight 40.32

T, °K.	ΔT approx.	C_p, cal./deg.	T, °K.	ΔT approx.	C_p, cal./deg.
20.34	2.9	0.0220	156.19	5.5	4.717
23.05	3.4	.0282	161.39	5.1	4.970
26.08	3.2	.0389	166.76	5.7	5.190
29.16	3.0	.0596	172.75	6.4	5.455
32.07	2.7	.0659	178.83	6.0	5.721
35.17	3.5	.0928	184.81	5.9	5.971
39.15	4.5	.1183	190.51	5.4	6.184
43.40	4.1	.1480	195.81	5.0	6.380
48.30	5.7	.2148	200.72	4.8	6.570
53.52	5.3	.2812	205.76	4.6	6.708
58.26	4.3	.3609	210.20	5.3	6.888
69.01	4.5	.6708	215.36	5.1	7.031
73.62	4.6	.8341	220.34	4.9	7.215
78.46	5.1	1.022	225.06	4.8	7.336
83.53	5.2	1.239	230.50	6.2	7.472
88.77	5.4	1.481	236.51	6.0	7.608
94.26	5.6	1.730	242.55	5.7	7.788
99.94	5.6	1.996	248.29	5.5	7.928
105.51	6.0	2.267	253.74	5.4	8.059
111.23	5.3	2.542	258.99	5.4	8.199
116.04	5.3	2.786	264.18	5.1	8.313
121.57	5.7	3.071	269.15	4.9	8.387
127.56	5.2	3.408	274.10	4.8	8.489
132.60	4.8	3.655	278.78	4.7	8.636
137.25	4.6	3.886	283.90	5.2	8.724
142.03	5.0	4.158	289.19	5.0	8.856
146.78	4.5	4.324	294.25	4.9	9.000
151.39	4.8	4.545	300.68	5.1	9.088

TABLE II

MOLAL HEAT CAPACITY OF MAGNESIUM HYDROXIDE

Molecular weight 58.34

T, °K.	ΔT approx.	C_p, cal./deg.	T, °K.	ΔT approx.	C_p, cal./deg.
22.07	2.8	0.1143	140.80	6.3	9.036
25.69	2.8	.1889	146.70	5.8	9.489
29.74	4.7	.3142	152.24	5.3	10.02
34.25	4.0	.4665	157.27	4.9	10.36
38.44	3.9	.6145	162.20	5.3	10.73
42.54	4.1	.7871	167.68	5.7	11.18
46.94	3.7	.9973	173.51	5.9	11.68
52.28	6.3	1.292	179.37	5.4	12.14
59.04	7.4	1.678	184.61	5.1	12.50
65.14	5.8	2.094	189.21	4.6	12.88
70.34	4.7	2.489	194.51	6.0	13.24
75.16	4.6	2.869	200.53	5.8	13.66
79.77	4.5	3.268	205.92	5.3	13.98
84.52	4.9	3.713	211.17	5.1	14.35
89.48	5.0	4.168	216.61	5.3	14.59
94.32	4.6	4.609	221.85	5.1	14.92
99.03	4.8	5.085	227.34	5.5	15.23
103.58	4.5	5.498	232.81	5.3	15.56
108.30	5.0	5.931	238.14	5.1	15.86
113.38	5.1	6.452	243.27	4.9	16.08
118.31	4.7	6.950	248.32	4.7	16.38
123.21	5.1	7.411	253.15	4.6	16.61
128.45	5.4	7.953	258.07	5.4	16.82
134.75	5.8	8.470	263.14	5.2	16.97
268.48	5.6	17.20	299.15	5.6	18.52
274.02	5.4	17.52	304.77	5.5	18.62
279.50	5.3	17.79	310.17	5.3	18.81
285.12	5.6	17.99	315.86	5.1	19.01
290.83	5.5	18.14	320.87	5.0	19.15
296.34	5.4	18.35			

nesium hydroxide. The extrapolated values used in the later calculations are included for this reason. A discussion of the probable error introduced by their extrapolation is given later.

The heat capacity of magnesium oxide has been measured at ordinary or higher temperatures by Regnault,[8] Russell,[9] Magnus,[10] McDowell and Howe,[11] Parks and Kelley,[12] and Wilkes.[13]

We have adopted the smoothed values given in the "I. C. T."[14] The curve through these values connects well with the curve through our data below 300°K.

TABLE III

MOLAL HEAT CAPACITIES OF $Mg(OH)_2$ AND MgO

Molecular weights 58.34 and 40.32. Values taken from smooth curves through the data. C_p in cal./deg. per mole.

T, °K.	MgO, C_p	$Mg(OH)_2$, C_p	T, °K.	MgO, C_p	$Mg(OH)_2$, C_p
20	0.021	0.082	200	6.537	13.62
30	.057	.320	210	6.880	14.24
40	.126	.676	220	7.182	14.83
50	.234	1.158	230	7.460	15.38
60	.397	1.740	240	7.707	15.92
70	.704	2.456	250	7.958	16.44
80	1.084	3.285	260	8.208	16.89
90	1.527	4.213	270	8.440	17.34
100	1.998	5.156	280	8.662	17.76
110	2.482	6.125	290	8.875	18.15
120	3.000	7.090	300	9.070	18.47
130	3.542	8.032	310	(9.20)	18.79
140	4.013	8.93	320	(9.34)	19.12
150	4.476	9.79	350	(9.65)	(19.97)
160	4.905	10.56	400	(10.00)	(21.28)
170	5.330	11.37	450	(10.34)	(22.55)
180	5.760	12.20	500	(10.62)	(23.68)
190	6.173	12.94			

The heat capacity of magnesium oxide has been measured at low temperatures by Günther[15] and by Parks and Kelley.[12] The measurements of Günther are not self-consistent and deviations from the present data range from 70 to 13% low over the interval 40 to 85°K.

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(8) Regnault, *Ann. chim. phys.*, **1**, 129 (1841).

(9) Russell, *Physik. Z.*, **13**, 59 (1912).

(10) Magnus, *ibid.*, **14**, 5 (1913).

(11) McDowell and Howe, *J. Am. Ceramic Soc.*, **3**, 185 (1920).

(12) Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

(13) Wilkes, *J. Am. Ceramic Soc.*, **15**, 72 (1931).

(14) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. V, 1926, p. 99.

(15) Günther, *Ann. Physik*, **51**, 828 (1916).

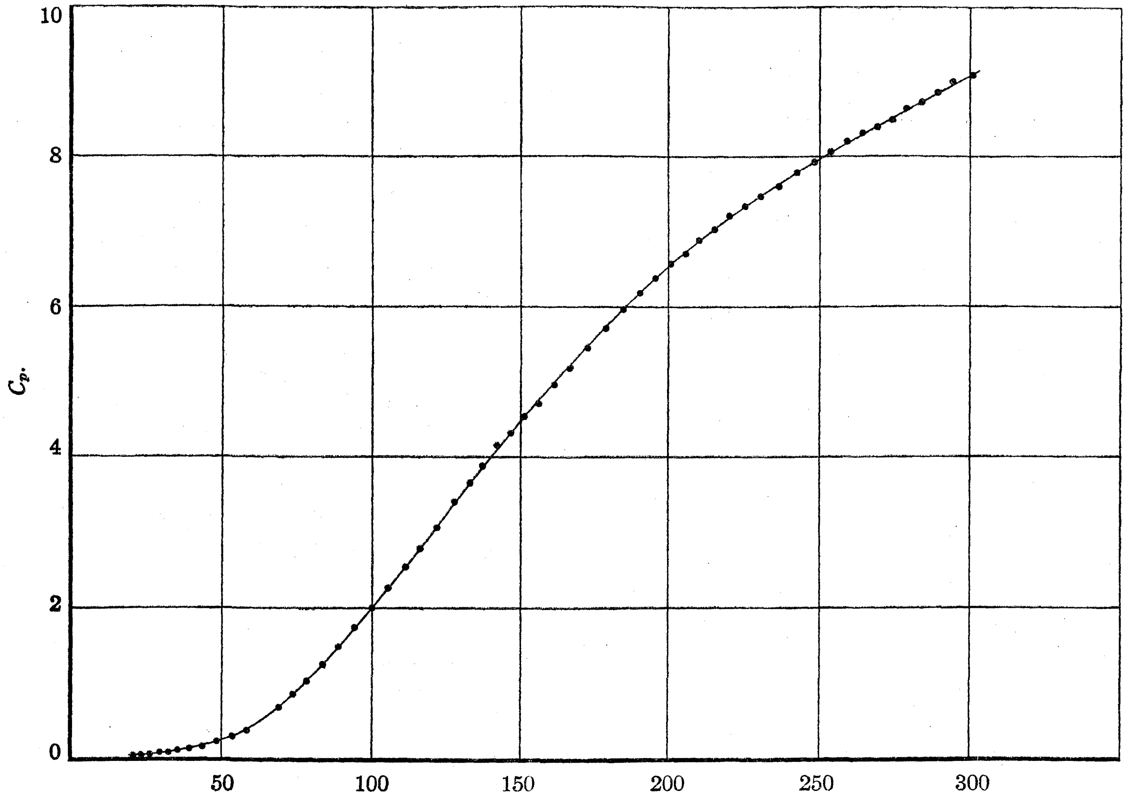

Fig. 2.—Molal heat capacity of magnesium oxide in calories per degree.

The measurements of Parks and Kelley over the range 90–290°K. fall on a smooth curve which lies about 1% below the present observations at ordinary temperatures with the difference increasing by systematically greater amounts at lower temperatures. At 90°K. the deviation has increased to −6%.

We do not question the accuracy of the measurements of Parks and Kelley, since some of their other measurements with the same calorimeter have been substantiated by the work of other observers. Thus the probable cause of the deviation deserves some comment.

The magnesium oxide used by Parks and Kelley had been crystallized from the fused oxide by the Norton Company. It was shown to be pure by analysis. We have learned in a personal communication from Dr. Kelley that cleavage planes of the crystal indicated it to be cubic and rather perfect in character. Also an x-ray investigation on some of the same material had shown typical Laue spot patterns.

As has been mentioned above, the magnesium oxide used in the present investigation was prepared by decomposing the hydroxide in a vacuum at 300–350°. This was considered desirable in order that we might have material in the same state as that in which it was present during the decomposition equilibrium. The material obtained in this manner was of course a powder and it appears that the difference in the results obtained by Parks and Kelley and in this research is due to the difference in the physical state of the material. The low temperature heat capacity results on the very poorly conducting finely divided magnesium oxide are not as accurate as those on the crystalline magnesium hydroxide but it seems probable that the present results on the oxide are too low rather than too high. The fact that the measurements are 6% higher than those of Parks and Kelley on large crystals of magnesium oxide at 90°K. is not so surprising when one considers that the actual difference is a little less than a tenth of a calorie per mole and that some of the molecular restraints must have been weakened on and near the very large amount of surface formed when the magnesium hydroxide was dehydrated.

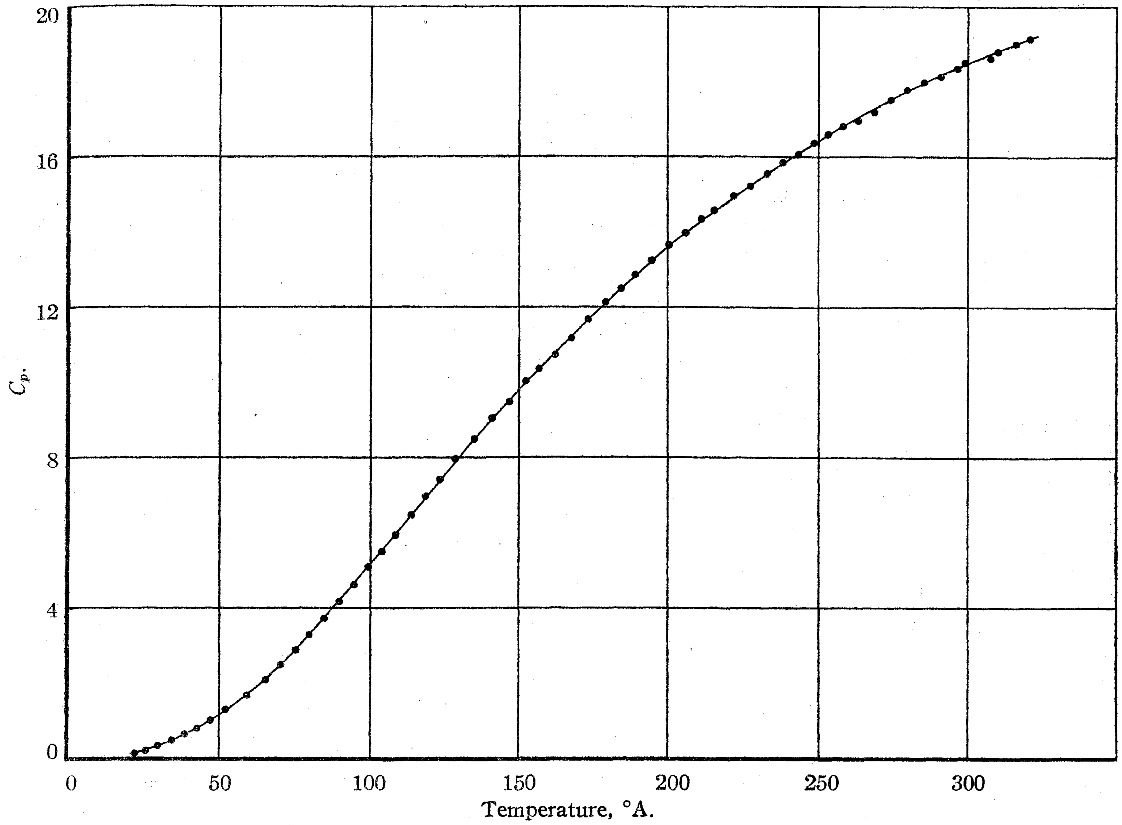

Fig. 3.—Molal heat capacity of magnesium hydroxide in calories per degree.

The Heat of Decomposition of Magnesium Hydroxide.—The heat of the reaction $Mg(OH)_2 = MgO + H_2O(l)$ was determined by measuring the heats of solution of magnesium hydroxide and magnesium oxide in dilute hydrochloric acid.

Figure 4 shows a cross-sectional diagram of the calorimeter used for the measurements of the heats of solution of magnesium oxide and magnesium hydroxide in hydrochloric acid. The apparatus consisted essentially of a dewar vessel equipped with a stirrer, a resistance thermometer and heater combined, and a means of admitting the sample. The one-liter silvered dewar vessel was specially made, without spacing plugs, to minimize heat leak. The resistance thermometer-heater, A, was wound on a platinum tube 2 cm. in diameter and 7 cm. long. It consisted of about 45 ohms of number 40 B. and S. gage double silk-covered copper wire insulated and kept in good thermal contact with the tube by Bakelite lacquer. A thin platinum sheath was put over this and welded around the ends. The leads of number 24 copper wire came through a small platinum tube welded to the inside tube of the thermometer-heater. Potential leads were attached at a point somewhat above the surface of the liquid in the dewar vessel, thus minimizing the effect of the heat generated in the leads. The thermometer-heater was supported by the small platinum tube.

Two different stirrers, B, were used at different times during the work. One was a 10-blade platinum stirrer, the other a 3-blade glass stirrer. These were fastened with deKhotinsky cement into the stirrer shaft well above the liquid level in the dewar vessel. The stirrer shaft was made from thin German silver tubing to minimize heat conduction. Bearing surfaces were provided only near the ends.

The upper framework of this calorimeter was a heavy support with a series of tubes leading down to the mouth of the dewar vessel. The joint between the support and the dewar was made water tight with adhesive tape and paraffin while the dewar flask was held snugly in place by a metal ring underneath attached to the upper metal part by three cords and a spring. The tubes were used as follows: one for the stirrer shaft; one for the thermometer-heater, E (this tube was filled with paraffin to keep the wires in thermal contact with the tube), and two for the sample tube. These tubes were made long to make sure that all heat leaking into the calorimeter through the various shafts and wires would be from the temperature of the outside bath.

The device for admitting the sample was constructed as follows: A glass tube, C, 5 cm. long and 1.5 cm. outside diameter was ground flat on both ends. A piece of thin gold foil was fastened over one end with paraffin. The sample was then weighed into the tube, after which the other end was sealed with gold foil. This tube was then fastened with adhesive tape and paraffin to one end of a glass rod which passes through one of the tubes in the upper framework of the calorimeter. In placing the dewar flask on the apparatus, the sample tube could be turned under the stirrer to pass the neck of the flask, then turned out and drawn up to its place beside the resistance thermometer. A pointed glass rod, D, passed through the other tube in the upper part of the apparatus and was held so that its point was about a millimeter directly above the sample tube. When it was desired to dissolve the sample, this glass rod was pushed through both pieces of gold foil, then pulled back to its original position.

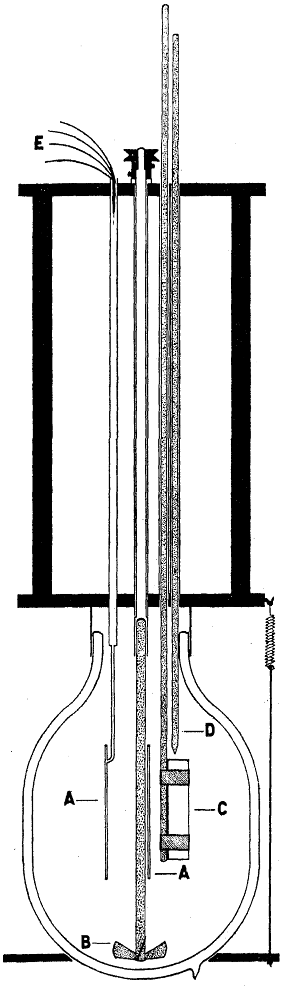

Fig. 4.—Calorimeter used for heat of solution measurements.

Resistance thermometer measurements were made with a Müller type Wheatstone bridge with a galvanometer of high sensitivity. When the bridge was in balance the current through the resistance thermometer was about 3 m. a. The small amount of heat resulting from the thermometer current was included in the "heat of stirring" correction. The stirrer was driven at constant speed to ensure constancy of this correction factor. The energy used for determining the heat capacity of the calorimeter was supplied by storage cells. The energy measurements were made with a Leeds and Northrup type K potentiometer.

The heat of solution measurements were arranged so that the various concentrations and amounts were the same in the final solution of every experiment. This solution was obtained by adding 5.0000 g. of magnesium hydroxide to 900 cc. of 1.0000 *N* hydrochloric acid. 1.461 g. of water was added to the acid solution before the magnesium oxide measurements.

The thermostat surrounding the calorimeter was kept at about 25°C. and the temperature was recorded to 0.001°. The experiments were arranged so that the bath temperature was midway between the initial and final calorimeter temperatures. Perhaps it would have been preferable to keep the calorimeter temperature always below that of the thermostat to eliminate any possibility of distillation heat effects. However, it may be shown that there was practically no tendency for distillation to occur in the present case. The affinity of water for hydrogen chloride is so great that it approximates the properties of a non-volatile solute in dilute solution. The vapor pressure of water over 1 *M* hydrochloric acid is sufficiently below that of pure water so that the solution must be about 0.7° above the thermostat temperature before a practicable mechanism for distillation becomes possible.

The correction for heat interchange with the surroundings was made graphically and it was assumed that the thermal leakage was at every instant proportional to the temperature difference between the bath and the calorimeter. The validity of this assumption for the present apparatus and conditions was carefully checked experimentally. Temperature readings were taken at minute intervals during the reaction period and the reaction was considered complete only when the observed rate of temperature change agreed with the value calculated from the known thermal head and the "heat of stirring." The oxide dissolved much more readily than the hydroxide and consequently the runs were shorter. The magnitude of the total heat corrections was about 1% of the heat of solution.

Several heat capacity determinations were made after each heat of solution experiment. These measurements were made with approximately the same temperature increase as that during solution and were made both at lower and higher temperatures so a good interpolated value could be obtained.

The 0.15% (0.22 mole %) potassium impurity is sufficient to require some consideration concerning its possible effect on the results. It may safely be assumed that it was present as potassium hydroxide and it would remain as potassium hydroxide when magnesium oxide was formed from the hydroxide. By coincidence, not only are the molecular weights of potassium and magnesium hydroxides nearly the same but their molal heats of solution are the same within a fraction of a per cent. Thus no appreciable error would have been introduced by ignoring the presence of the potassium hydroxide in the pure magnesium hydroxide, or by counting it as magnesium hydroxide in the magnesium oxide. The heat of solution of magnesium hydroxide to be given later was obtained by making the above assumption. However, in determining the heat of dehydration of magnesium hydroxide we made the better assumption that the heat of solution of the potassium hydroxide would cancel in obtaining the difference of the two experimental values. The experimental values are given in Table IV.

TABLE IV

HEATS OF SOLUTION OF "$Mg(OH)_2$" AND "MgO" IN *M* HCl AT 25°C.

5.0000 g. "$Mg(OH)_2$" = 0.085526 mole $Mg(OH)_2$ + 0.000192 mole KOH. 3.5386 g. "MgO" = 0.081119 mole MgO + 0.004407 mole $Mg(OH)_2$ + 0.000192 mole KOH. Molecular weights: $Mg(OH)_2$ = 58.336, MgO = 40.32.

Experiment	"$Mg(OH)_2$"	"MgO"
1	2294.2	3084.1
2	2293.5	3082.4
3	2294.7	3085.5
Mean	2294.1	3083.8

From Table IV it is found that the dehydration of 0.081119 mole of magnesium hydroxide requires 3083.8 − 2294.1 = 789.7 cal. The corresponding value is 9735 cal./mole of magnesium hydroxide. From the data of Rossini[16] we estimate that the

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[16] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

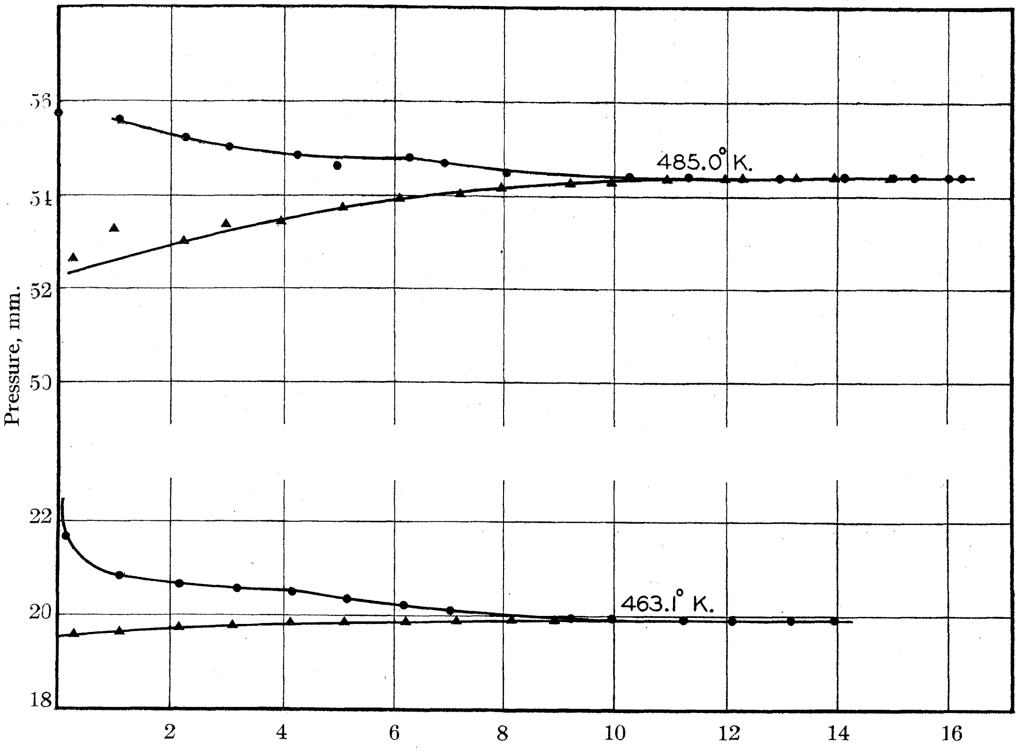

Fig. 5.—The dissociation pressure, showing the approach to equilibrium.

partial molal heat content of water in the final calorimetric solution is 4 cal. less than that of pure water. Applying this correction

$$Mg(OH)_2 = MgO + H_2O(l) \quad \Delta H_{298.1} = 9739 \text{ cal.}$$

Also

$$Mg(OH)_2 + 10{,}500 \text{ cc. } M \text{ HCl} = \text{Solution} + 26{,}763 \text{ cal.}$$
$$MgO + 1 \text{ mole } H_2O \text{ in } 10{,}500 \text{ cc. } M \text{ HCl} = \text{Solution} + 36{,}498 \text{ cal.}$$

The Dissociation Pressure of Magnesium Hydroxide.—The apparatus used to measure the dissociation pressure of magnesium hydroxide was a manometer, of 1.5-cm. inside diameter glass tubing, with a bulb on one side containing a mixture of magnesium hydroxide and magnesium oxide. The other side of the manometer was connected through a mercury U-trap to a high vacuum system. The manometer, sample bulb and U-trap were kept in a stirred air thermostat which could be kept constant to 0.1° at any temperature up to 220°C.

Both sides of the manometer and the sample were pumped, by means of a mercury diffusion pump with a liquid air trap in the line. The sample and line were at a temperature of about 200°C. during the evacuation. The sample bulb side was then sealed off. The mercury could be run up in the U-trap thus allowing the vapor pressure of mercury on the vacuum side of the manometer to balance that on the bulb side. The U-trap also served to prevent distillation of the mercury from the manometer to the vacuum line outside the thermostat. This is an important consideration in cases such as the present one where the rate of change of pressure due to volume change on the bulb side, because of loss of mercury, would have been of the same order as the rate of change during approach to equilibrium. The difference in height of the mercury menisci was read through a plate glass window by means of a cathetometer accurate to a few hundredths of a mm.

Equilibrium pressures were obtained at 463.1 and 485.0°K. In each case the equilibrium was approached from both higher and lower temperatures. Table V gives the pressures measured during the approach to equilibrium. Each observation given is an average of several measurements. The individual readings did not vary more than 0.1 mm. from the average. The pressures are given in international cm. of mercury. In correcting the observations the density of mercury was taken from the "I. C. T."[17] The standard acceleration of gravity was taken as 980.665 cm./sec.^{2}. The gravitational acceleration at this location has been determined by Sternwarte[18] as 979.973 cm./sec.^{2}. The data are represented graphically in Fig. 5.

The first flat portion in the curves approaching equilibrium from high pressures is attributable to adsorption. That this might easily have been mistaken for true equilibrium is shown by the following experiment. During some preliminary measurements the apparatus was cooled while the approach to equilibrium was in the adsorption stage. On return to the original temperature there was a return to the false equilibrium value and later a decrease to

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[17] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926.

[18] Sternewarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Verlag Julius Springer, Berlin, 1928.

the true equilibrium pressure. It is quite evident that approach to the same pressure from each side of an equilibrium is not a sufficient criterion of true equilibrium. The effect is so insidious that we have little doubt that many such errors have occurred in the study of equilibria. A case in point are the previous data[19] on the dissociation pressure of magnesium hydroxide. These measurements are so badly in error that we were led to believe that the dissociation pressure could be measured conveniently at temperatures obtainable with a water thermostat and we set up such an apparatus. It soon became clear that the dissociation pressure measurements of Johnston over the system magnesium hydroxide and magnesium oxide were in reality adsorption pressures and calculation of the heat of reaction from the data showed a value of the same order as the heat of vaporization of water.

TABLE V

DISSOCIATION PRESSURES OF $Mg(OH)_2$

Approaching equilibrium from low pressures				Approaching equilibrium from high pressures			
463.1°K.		485.0°K.		463.1°K.		485.0°K.	
Time, days	P inter. cm.	Time, days	P inter. cm.	Time, days	P inter. cm.	Time, days	P inter. cm.
0.29	1.954	0.25	5.263	0.13	2.164	0	5.570
1.08	1.964	.96	5.326	1.08	2.082	1.08	5.558
2.13	1.971	2.21	5.301	2.15	2.064	2.25	5.522
3.08	1.976	2.96	5.336	3.17	2.055	3.00	5.503
4.13	1.983	3.94	5.341	4.17	2.049	4.25	5.485
5.08	1.985	5.04	5.371	5.15	2.033	4.96	5.462
6.21	1.987	6.08	5.391	6.17	2.022	6.29	5.481
7.13	1.989	7.19	5.401	7.04	2.009	6.92	5.472
8.13	1.991	7.96	5.416	9.21	1.994	8.04	5.448
8.96	1.991	9.21	5.426	9.96	1.994	10.25	5.441
		9.94	5.426	11.21	1.991	11.29	5.437
		10.94	5.436	12.08	1.991	12.96	5.439
		11.96	5.439	13.13	1.991	14.13	5.439
		12.27	5.438	13.96	1.991	15.00	5.439
		13.25	5.440			15.37	5.438
		13.92	5.437			16.00	5.439
		14.87	5.439			16.25	5.439
Equil. values	1.991		5.439		1.991		5.439

Thermodynamic Treatment of the Data.—Various thermodynamics quantities of interest to the experiment are tabulated in Table VI. They were obtained from data relating to the reactions

$$Mg(OH)_2 = MgO + H_2O(l) \qquad (2)$$

$$H_2O(l) = H_2O(g) \qquad (3)$$

$$Mg(OH)_2 = MgO + H_2O(g) \qquad (4)$$

$\Delta F^\circ = -RT \ln K$ where K is the vapor pressure (in atm.) of water in equation 3 and the dissociation pressure (in atm.) in equation 4.

$$\Delta H_T = \Delta H_{298.1} + \int_{298.1}^{T} \Delta C_p \, dT$$

$$\Delta S_T = (\Delta H - \Delta F)/T$$

$$\Delta S_{298.1} = \Delta S_T - \int_{298.1}^{T} \Delta C_p \, d \ln T$$

The heat of vaporization of water at 298.1°K., ΔH of equation 3, has been estimated as 10,499 ± 3 cal. per mole by Giauque and Stout[2] after a consideration of the very accurate available data which have been reviewed by Fiock.[20]

Thermodynamic quantities including the heat content and entropy of gaseous water have been calculated from spectroscopic data by Gordon[21] and these values were used where necessary. However, corrections for the rotational deformation of the water molecule were applied to Gordon's values in accordance with the calculations of Wilson.[22]

The entropies of magnesium hydroxide and oxide were obtained from the third law of thermodynamics by graphical integration of the heat capacity data

$$S = \int_0^T C_p \, d \ln T$$

Since the heat capacity of magnesium hydroxide was extrapolated for about 150° above the last measurement, at 320°K., the probable error due to this assumption requires comment. While we believe the extrapolation is reliable, we wish to point out that considerable error in the assumed values would produce little effect in the final result. For example let us consider the effect of an error of one calorie per degree in the assumed heat capacity at 475°K. The curve at 320°K. gives direction as well as value to the curve above that temperature, thus a reasonable type of deviation would be given by a proportionality to the square of the temperature difference above 320°K. Since the same heat capacity values are used for calculating differences in heat content and in entropy the effect of an error in the assumed heat capacity values largely cancels. It may be shown that a deviation of the above type will increase the derived entropy of water by approximately 0.01 cal./deg. per mole for each increase of one calorie per degree in the

TABLE VI

SOME THERMODYNAMIC QUANTITIES RELATED TO THE EQUILIBRIUM

$Mg(OH)_2 = MgO + H_2O(g)$

T, °K.	ΔF	ΔH	ΔS	MgO, S_T	$Mg(OH)_2$, S_T	H_2O, S_T Exptl.	H_2O, S_T Spect.
485.0	2541	19,689	35.36	11.47	25.22	49.11	49.10
463.1	3351	19,783	35.48	10.98	24.15	48.65	48.72
298.1	9297	20,238	36.67	6.66	15.09	45.10	45.13

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(19) Johnston, *Z. physik. Chem.*, **62**, 330 (1908).

(20) Fiock, *Bur. Standards J. Research*, **5**, 481 (1930).

(21) Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(22) Wilson, *ibid.*, **4**, 526 (1936).

heat capacity of magnesium hydroxide at 475°K. Thus error introduced by the extrapolation can be estimated at not more than a few hundredths of an entropy unit.

The experimental entropy value given for 298.1°K. was calculated from an average of the measurements at 463.1 and 485.0°K.

As may be seen from the comparisons in the last two columns of Table VI the third law values of the entropy of water are in excellent agreement with those calculated from the band spectrum data.

We thank Dr. Roy Overstreet for analyzing the magnesium hydroxide used in the above experiments.

Summary

The heat capacities of magnesium oxide and magnesium hydroxide have been measured from 20 to 300°K. and 20 to 320°K., respectively.

Evidence has been presented to show that the low temperature heat capacity of magnesium oxide prepared by the decomposition of magnesium hydroxide at 300–350°C. is definitely greater than the heat capacity of crystalline material prepared from the fused oxide.

The dissociation pressure of the system $Mg(OH)_2$, MgO has been measured accurately at 463.1 and 485.0°K. The pressures found were 1.991 and 5.439 international cm., respectively.

During the dissociation measurements it was found that an approach to the equilibrium from the high temperature side was at first accompanied by a slowly obtained false equilibrium pressure due to surface adsorption of the water. If the substance was cooled at this stage it was possible to approach the same false equilibrium from the low temperature side. It is evident that this usual experimental criterion for true equilibrium in such cases is by no means a safe one.

It is suggested that dissociation equilibria should be first approached from the low temperature side. Subsequent attainment of the same value from the high temperature direction may be taken as substantial evidence of true equilibrium.

The heat of solution of one mole of magnesium hydroxide in 10,500 cc. of molal hydrochloric acid was found to be 26,763 calories at 25°C.

The heat of solution of one mole of magnesium oxide in 10,500 cc. of molal hydrochloric acid +1 mole of water was found to be 36,498 calories at 25°C.

These measurements when corrected for the partial molal heat content of water in the solution lead to a value of $\Delta H_{298.1°\text{K.}} = 9738$ cal. for the dissociation of one mole of magnesium hydroxide to give magnesium oxide and pure liquid water.

The above data have been used with the third law of thermodynamics to calculate the molal entropy of gaseous water at 485.0, 463.1 and 298.1°K. The values obtained are 49.11, 48.65 and 45.10 cal./deg., respectively.

These may be compared with values obtained with the assistance of the band spectrum data for water. The values for corresponding temperatures are 49.10, 48.72 and 45.13 cal./deg., respectively.

The excellent agreement constitutes one of the best pieces of evidence in support of the third law of thermodynamics and of the results of quantum statistics.

The free energy for the dissociation of magnesium hydroxide is

$$Mg(OH)_2 = MgO + H_2O(g) \quad \Delta F_{298.1°\text{K.}} = 9297 \text{ cal./mole.}$$

BERKELEY, CALIF. RECEIVED DECEMBER 24, 1936

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

Double Compounds of Urea with Magnesium Nitrate and Magnesium Sulfate

BY J. Y. YEE, R. O. E. DAVIS AND S. B. HENDRICKS

In the course of an investigation of new fertilizer materials several new double compounds of urea with magnesium salts were obtained. Urea is quite hygroscopic at high humidities and also has the tendency to form double compounds. This tendency is sometimes a disadvantage in fertilizer mixtures, when urea displaces water of crystallization in forming a double compound with other constituents in the mixtures. Such a reaction has been attributed by Whittaker, Lundstrom and Hendricks[1] as the cause of stickiness encountered sometimes in fertilizer mixtures containing urea. The possibility was suggested that double compounds suitable for fertilizers might be obtained, which would be less hygroscopic than urea and also would not react further in mixtures to release free water from hydrated salts. A number of double compounds of urea are known, such as $Ca(NO_3)_2 \cdot 4CO(NH_2)_2$, $CaSO_4 \cdot 4CO(NH_2)_2$;[1] $SrBr_2 \cdot CO(NH_2)_2$,[2] etc.; and in some cases these render the urea in combination less hygroscopic.

The compound $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$ has been reported recently by Whittaker, Lundstrom and Shimp[3] of this Laboratory, in their study of the system magnesium sulfate–urea–water at 30°. This was formed from water solution while the sulfate compounds reported here were formed from alcoholic solution. In treating magnesium salts with urea in this manner three new double compounds were prepared and because of their high urea content, they were considered a potential source of nitrogen in fertilizers.

Preparation of New Double Compounds

The chemical compositions and the crystal properties of the new double compounds have been studied, but their physical condition and behavior in mixed fertilizer are still under investigation. One of these double compounds is a combination of urea and magnesium nitrate and the other two are of urea and sulfate in different proportions. They are represented by the formulas:

$$Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$$
$$MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$$
$$MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$$

Double Compound, $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$.—The nitrate double compound was prepared from equal parts (100 g. each) of the solids magnesium nitrate hexahydrate and urea by the following procedure. At first the crystalline nitrate and urea were mixed in small amounts in ratio of about 8 to 1 in a tube maintained at about 55°. After the appearance of a liquid phase, further amounts of the two salts were added slowly with gentle stirring in about the same proportion. When all the magnesium nitrate had been added, the resulting liquid was quite clear. The remainder of the urea was then introduced gradually. After removal of the tube from the bath, fine crystals came down with stirring and were separated from the mother liquor at room temperature. About 100 g. of the product was obtained from 100 g. each of magnesium nitrate hexahydrate and urea.

Larger individual crystals of this double compound for x-ray diffraction photographs were obtained by dissolving 30 g. of magnesium nitrate hexahydrate and 40 g. of urea in 30 cc. of ethyl alcohol at 40°. On standing at 20° well-formed crystals of $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$ were obtained.

Double Compound, $MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$.—This compound was obtained as individual orthorhombic crystals from methyl alcohol solution. One gram of powdered magnesium sulfate heptahydrate was dissolved in 20 cc. of methyl alcohol in a crystallizing dish (9 cm. in diameter). To this solution, 2.5 g. of finely powdered urea was added. On gently stirring the solution, or by slowly rotating the dish, the urea was dissolved completely. With the dish tightly covered to prevent evaporation of the alcohol, clear crystals of the compound formed on standing at 30°.

Double Compound, $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$.—This compound, when prepared from absolute methyl alcohol solution, formed polycrystalline masses with clear clusters of crystals. Clear, individual crystals, however, were prepared from 95% methyl alcohol solution. Two grams of powdered magnesium sulfate heptahydrate was dissolved in 25 cc. of 95% methyl alcohol in a crystallizing dish (9 cm. in diameter). To this was added 4 g. of powdered urea. On gently stirring the solution, or rotating the dish, the urea was dissolved completely. With the dish tightly covered, individual crystals formed on standing at room temperature, about 25°.

The similarity of conditions for formation of the two magnesium sulfate–urea compounds is quite striking, but the concentrations of solutions are different in the two cases. At the particular ratio of the salts used in preparing the six urea compound, individual crystals were obtained from 95% methyl alcohol, while polycrystalline masses only were obtained from absolute methyl alcohol.

Examination of the Compounds.—Chemical analyses were made and x-ray and optical properties were determined for the three compounds. The molecular weights of all three compounds, derived from the x-ray diffraction data, are in positive agreement with the values calculated from the chemical analyses. It is of interest to note that

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(1) Whittaker, Lundstrom and Hendricks, *Ind. Eng. Chem.*, **25**, 1280 (1933).

(2) DeCarl, *Atti accad. Lincei*, **15**, 747 (1932).

(3) Whittaker, Lundstrom and Shimp, THIS JOURNAL, **58**, 1975 (1936).

the densities obtained for $Mg(NO_3)_2{\cdot}4CO(NH_2)_2{\cdot}2H_2O$ and $MgSO_4{\cdot}5CO(NH_2)_2{\cdot}2H_2O$ are identical within the limits of experimental error. Analyses for urea by the Yee and Davis urease method[4] and for magnesium by the magnesium ammonium phosphate method gave results checking consistently with calculated values for the three compounds. Some of the results are shown in Table I.

TABLE I

COMPOSITION OF THE DOUBLE COMPOUNDS OF UREA

Double compounds		$Mg(NO_3)_2{\cdot}$ $4CO(NH_2)_2{\cdot}$ $2H_2O$	$MgSO_4{\cdot}$ $5CO(NH_2)_2{\cdot}$ $2H_2O$	$MgSO_4{\cdot}$ $6CO(NH_2)_2{\cdot}$ $2H_2O$
Mol. wt.	Calcd.	424.56	456.65	516.69
	Obsd.[a]	422.0	457.75	514.00
Urea, %	Calcd.	56.56	65.75	69.73
	Found	56.32	65.69	69.86
Mg, %	Calcd.	5.73	5.33	4.71
	Found	5.72	5.37	4.79
Total N calcd.		32.99[b]	30.68	32.53

[a] From measurements of the lattice constants by means of x-ray diffraction

$$\frac{\text{Mol. wt.}}{\text{Density}} = \frac{a \times b \times c \times \cos\beta \times \text{Avogadro's number}}{\text{No. of formula weights in the unit}}$$

[b] 26.4% urea nitrogen and 6.6% nitrate nitrogen.

Optical and x-Ray Examination.—Results of x-ray and optical measurements on the various salts are listed in Table II. Refractive index values are useful both for identification and for structure analysis. Measurements of the lattice constants combined with the density leads directly to the molecular weight, as listed in Table I, and thus to a check on the analytical data.

TABLE II

OPTICAL AND x-RAY DIFFRACTION DATA FROM SOME DOUBLE UREA COMPOUNDS WITH MAGNESIUM SALTS

Compounds		$Mg(NO_3)_2{\cdot}$ $4CO(NH_2)_2{\cdot}$ $2H_2O$	$MgSO_4{\cdot}$ $5CO(NH_2)_2{\cdot}$ $2H_2O$	$MgSO_4{\cdot}$ $6CO(NH_2)_2{\cdot}$ $2H_2O$
Crystal symmetry and common forms		Monoclinic prismatic, (011), (010), (110)	Rhombic dipyramidal (101), (111)	(110), (111)
Space group		C_{2h}^5 – $P2_1/n$	D_{2h}^{16} – $Pnma$	D_{2h}^{10} – $Pccn$
Lattice dimensions, Å.	a	6.38	17.32	16.20
	b	18.10	11.40	19.97
	c	7.55	9.61	14.38
β		93°20′		
Form. wts. in unit		2	4	8
Refractive indices	α	1.393	1.515	1.493
	β	1.539	1.533	1.508
	γ	1.595	1.551	1.520
Density		1.596	1.596	1.458

Refractive indices were measured by the immersion method. x-Ray powder diffraction photographs, rotating crystal and equatorial zone Weissenberg photographs, about the crystallographic axes, were obtained for the three compounds; CuK radiation being used. Densities were determined by the Retger suspension method. None of the compounds is piezoelectric.

Since there are only two $Mg(NO_3)_2{\cdot}4CO(NH_2)_2{\cdot}2H_2O$ in the monoclinic prismatic unit of structure, it follows that the magnesium atoms must be in unique positions. In the space group $P2_1/n$ they are at symmetry centers about which the urea and water molecules are repeated. It thus is probable that the four oxygen ends of the urea molecules and the two water molecules are grouped around magnesium at the corners of an octahedron, giving magnesium a coördination number of six. The plane of the optic axes is (010) with the acute bisectrix 50° from the a axis and the low value of α suggests that the direction of vibration is approximately normal both to the planes of the nitrate and urea group, which planes would thus be parallel.

The space group of $MgSO_4{\cdot}5CO(NH_2)_2{\cdot}2H_2O$ requires the sulfate groups to be on symmetry planes which also contain one and possibly three urea molecules. It cannot be said whether $5CO(NH_2)_2$ and $2H_2O$ have their oxygen ends toward Mg or whether only $4CO(NH_2)_2{\cdot}2H_2O$ are so arranged. The birefringence of this compound is very low compared with that of the nitrate. This is also true of $MgSO_4{\cdot}6CO(NH_2)_2{\cdot}2H_2O$, which in addition must have a very complex structure as indicated by the large number of formula weights in the unit.

The authors wish to express their thanks to M. E. Jefferson of this Laboratory for making the refractive index measurements.

Summary

Three new double compounds of urea with magnesium salts have been prepared, and the methods of preparation described.

Two of the compounds are with magnesium sulfate and one with magnesium nitrate. Their compositions are represented by the formulas $MgSO_4{\cdot}5CO(NH_2)_2{\cdot}2H_2O$, $MgSO_4{\cdot}6CO(NH_2)_2{\cdot}2H_2O$ and $Mg(NO_3)_2{\cdot}4CO(NH_2)_2{\cdot}2H_2O$; and they contain 65.7, 69.7 and 56.5% of urea, respectively. The first two contain more urea than any of the previously known double salts.

x-Ray and optical examinations have been made of the compounds and the properties have been given. From x-ray diffraction data the molecular weights of the compounds have been calculated and found to agree closely with those derived from the chemical analyses.

Their physical properties and behavior when mixed in fertilizers have not yet been determined.

WASHINGTON, D. C. RECEIVED SEPTEMBER 18, 1936

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(4) Yee and Davis, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 259 (1935).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Relative Acid Strengths in Normal Butyl Alcohol[1]

BY R. BURGESS MASON AND MARTIN KILPATRICK

The study of acid strengths in non-aqueous solvents has necessitated a more critical use of the colorimetric method. This paper is a report of the use of a photoelectric colorimeter in the determination of acid strengths in the basic solvent *n*-butyl alcohol. A recent report of relative strengths of acids in this solvent by an electrometric method affords a basis for comparison of the two methods.[2]

Indicators behave just as do other acids and bases and the protolysis constant for the transfer of a proton from the acid A to the basic form of the indicator I_B to give the acid form of the indicator I_A and the base B is written

$$K_{A_1I_B} = C_{B_1}C_{I_A}/C_{A_1}C_{I_B} \qquad (1)$$

For the reverse reaction we would have $K_{I_AB_1}$ as the acid is written first.

The concentration of the acid or basic form of the indicator can be determined colorimetrically and $K_{A_1I_B}$ computed from the stoichiometric concentrations. From the protolytic constants with indicators the classical dissociation constants or the protolytic constants of a series of acids referred to a common base (in this case the solvent) can be obtained.

Upon addition of hydrogen chloride to the weak base normal butyl alcohol the reaction

$$\mathrm{HCl} + \mathrm{ROH} \longrightarrow \mathrm{ROH{\cdot}H^+} + \mathrm{Cl^-} \qquad (2)$$

probably goes practically to completion and we can take the concentration of $\mathrm{ROH{\cdot}H^+}$ as equal to the stoichiometric concentration of the hydrochloric acid. This assumption is in agreement with the results of catalytic studies by Brönsted and Vance[3] who show that both hydrochloric and hydrobromic acids are probably practically completely dissociated in isoamyl alcohol. The reaction with the indicator base is

$$\mathrm{ROH{\cdot}H^+} + \mathrm{I_B} \rightleftarrows \mathrm{ROH} + \mathrm{I_A} \qquad (3)$$

for which the protolysis constant is

$$K'_{(\mathrm{ROH\cdot H^+})\mathrm{I_B}} = C_{\mathrm{ROH}}C_{\mathrm{I_A}}/C_{(\mathrm{ROH\cdot H^+})}C_{\mathrm{I_B}} \qquad (4)$$

Now, since the concentration of the solvent is practically constant, this equation becomes

$$K_{(\mathrm{ROH\cdot H^+})\mathrm{I_B}} = C_{\mathrm{I_A}}C_{\mathrm{I_B}}C_{\mathrm{ROH\cdot H^+}} \qquad (5)$$

It follows from (1) and (5) that the protolysis constant of any acid and the solvent *n*-butyl alcohol may be expressed by the equation

$$K_{\mathrm{A(ROH)}} = \frac{K_{\mathrm{AI_B}}}{K_{(\mathrm{ROH\cdot H^+})\mathrm{I_B}}} = \frac{C_{\mathrm{B}}C_{\mathrm{I_A}}}{C_{\mathrm{A}}C_{\mathrm{I_B}}}\,\frac{C_{\mathrm{I_B}}C_{\mathrm{ROH\cdot H^+}}}{C_{\mathrm{I_A}}} = \frac{C_{\mathrm{B}}C_{\mathrm{ROH\cdot H^+}}}{C_{\mathrm{A}}} \qquad (6)$$

If an indicator is very sensitive to acids it is impossible to determine $K_{(\mathrm{ROH\cdot H^+})\mathrm{I_B}}$ with accuracy, and if the indicator is not very sensitive to acids it is equally impossible to determine $K_{\mathrm{AI_B}}$ with precision if the acid is weak. This difficulty is overcome by a stepwise procedure. $K_{\mathrm{A(ROH)}}$ can be determined for an acid with an indicator which is fairly insensitive to acids. With this value another indicator more sensitive toward acids is used and $K_{(\mathrm{ROH\cdot H^+})\mathrm{I_B}}$ for this second indicator is found, and now with another acid, A_1, and this same indicator, $K_{\mathrm{A_1(ROH)}}$ is computed from the experimentally determined $K_{\mathrm{A_1I_B}}$. A continuation of this stepwise procedure makes possible the evaluation of acidity constants that could not be reached by direct measurement.

Experimental Procedure

All colorimetric determinations of acid strength were carried out by measuring the concentration of a colored form of the indicator and then by substitution in equation (1), $K_{\mathrm{AI_B}}$ was found. With $K_{(\mathrm{ROH\cdot H^+})\mathrm{I_B}}$ determined by means of previous measurements, $K_{\mathrm{A(ROH)}}$ was evaluated.

The colorimetric determinations were based directly upon Beer's law, which states that the light transmitted by a solution is an exponential function of the thickness of the solution and of the concentration of the light-absorbing molecules. This expressed mathematically is

$$I_{\mathrm{T}} = I_0e^{-kcx} \qquad (7)$$

where I_{T} is the transmitted light, I_0 the incident light, e the natural base of logarithms, k a constant, c the concentration of the light-absorbing molecules and x the thickness of the solution through which the light traveled. Here it should be emphasized that this equation is applicable for light of one and only one wave length. The extinction coefficient k has a definite value for each particular wave length and if any agreement with Beer's law is to be expected, which in turn means great accuracy for the determinations, only monochromatic light should be used.

In order to have the readings free from personal error a photoelectric colorimeter was constructed. Approximately monochromatic light was obtained by passing light from an automobile head lamp, operated by a six-volt

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[1] Abstracted from the dissertation of Ralph Burgess Mason presented December 1, 1935, to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Wooten and Hammett, THIS JOURNAL, **57**, 2289 (1935).

[3] Brönsted and Vance, *Z. physik. Chem.*, **A163**, 240 (1932).

storage battery, through a Hilger constant deviation spectroscope. This source was used in preference to a lamp operating on the a. c. line because its intensity was more constant, since Partridge[4] has shown that one of the greatest limitations of the photoelectric cell is the variable voltage of the light source. He states that the intensity of a tungsten filament lamp is

$$I = kv^{3.6}$$

where I is the intensity, k a constant and v the voltage across the lamp. This equation shows that a large change in light intensity results from a small change in voltage, which means a large variation in the photoelectric current also.

The prism was on a turntable and by turning a calibrated drum a beam of light of any wave length could be obtained. The prism was first adjusted at 5890 and 6705 Å. by means of sodium and lithium flames. The light obtained from the incandescent bulb was approximately monochromatic (covering a range of 30 Å. units) after resolution by the prism.

The light from the spectrometer passed through the solution cell to the photoelectric cell, and as shown in Fig. 1 photoelectric currents were amplified by means of the amplifier of Razek and Mulder.[5] The solution cell was a quartz cell with clear quartz end-plates which were not sealed to the cylindrical part of the cell but were ground to fit. By means of an outer metal jacket the end-plates were held in place making a liquid-tight container. It was possible to have varying lengths of cell simply by removing an end-plate and attaching an extension to a 2-cm. tube. The extension had a concave grind at one end, a convex at the other and the concave grind fitted into the convex grind at the end-plate, the convex into the concave grind of the 2-cm. cell. With extensions it was possible to obtain cell lengths of 2, 4, 6, 8 and 10 cm. Most of the work, however, was carried out in the 2-cm. section.

Two types of photoelectric cells were used, a potassium hydride which is sensitive in the blue portion of the spectrum, and a cesium cell which has its maximum sensitivity in the longer wave lengths of the spectrum. These cells were housed in a copper box and were so arranged that the cesium cell could be used for yellow or red light and the potassium hydride cell for blue light. Neither of these cells shows much response to green light.

The apparatus was balanced by adjusting P_1 and P_2 so that the milliammeters would read the same (5 or 6 m. a.), and with the galvanometer fully protected by the galvanometer shunt R_G the switch was closed. Now by gradually increasing R_G more current flowed through the galvanometer causing a deflection. When this took place the plate currents of the two tubes were not the same but were brought into better adjustment by the variable resistance R′, and for very fine balance the variable resistance R was employed. The apparatus balanced by this means did not remain so unless the filament voltages of the two tubes were compensated, which was brought about by fixing the settings of the resistors at P_7 and P_8 and by finding the points where a small change in the setting of P_9 would result in no change of the galvanometer reading. With the apparatus thus balanced and adjusted it was ready for use. When the photoelectric voltage was superimposed on the grid of one tube, the galvanometer showed a deflection which was proportional to the photoelectric current which in turn was proportional to the intensity of the light striking the photoelectric cell. Although the galvanometer readings were only relative and not absolute measurements of the light intensity, nevertheless these deflections could be used to obtain the concentrations of the colored forms of the indicators, as will now be shown. Equation (7) may be put into the form

$$\log I_T = \log I_0 - (kcx/2.3) \qquad (8)$$

If Beer's law is obeyed the logarithm of the intensity of the transmitted light will be found to be a linear function of c, the concentration of the light-absorbing substance. The slope of the line is $-kx/2.3$. Since the galvanometer readings are proportional to the intensity of the light striking the photoelectric cell, galvanometer readings may be plotted as ordinates in place of I_T.

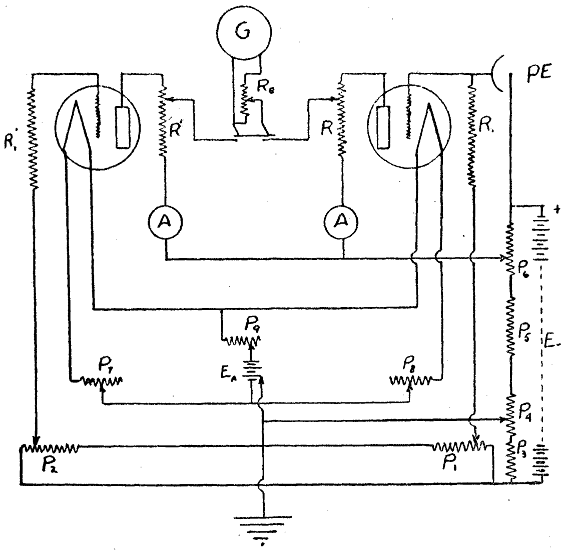

Fig. 1.—Electric circuit, meaning of symbols: A, milliammeters (10-m. a. range); G, Leeds and Northrup type R galvanometer No. 2500e; R_G, variable resistor, 1500 ohms; R_1, resistor, 100 megohms; R_1', resistor, 100 megohms; R, resistor, total of 1030 ohms (1000 ohms with variable portion of 30 ohms); R′, resistor, total of 1100 ohms (850 ohms with variable portion of 250 ohms); P_1 and P_2, potentiometers, 3000 ohms each; P_3, potential divider, 1500 ohms; P_4, potential divider, 1500 ohms; P_5, potential divider, 7000 ohms; P_6, potential divider, 3000 ohms; P_7 and P_8, variable resistors, 6 ohms each; P_9, variable resistor, 1 ohm; E_A, filament battery (6-volt storage); E_T, six 45-volt B batteries connected with two series of three in parallel; Cunningham 112A vacuum tubes were used.

The experimental procedure consisted of making one form of the indicator at various concentrations, which was done by preparing indicator solutions of the desired concentration and then adding a sufficient quantity of acid or base to produce the completely acidic or basic form of the

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(4) H. M. Partridge, *Ind. Eng. Chem., Anal. Ed.*, **2**, 207 (1930).

(5) Joseph Razek and P. J. Mulder, *J. Opt. Soc. Am.* and *Rev. Sci. Instruments*, **19**, 390 (1929).

indicator. The necessary amount of acid or base was determined experimentally, that is, acid or base was added to the indicator solution until an additional amount caused no change in the galvanometer reading. The basic forms of brom phenol blue and brom cresol green were solutions of their lithium salts, while the basic form of picric acid was prepared by the addition of lithium butylate until an increase of one drop caused no color change in the solution. The basic forms of brom cresol green, brom phenol blue and picric acid were used and the acidic forms of dimethyl yellow and benzene-azodiphenylamine. Different amounts of the colored form of each of these indicators were put into the solution cell, light passed through and the galvanometer read. The logarithms of these readings plotted against the concentration, lay on a straight line as required by Beer's law. From such curves the concentration of the colored form of the indicator in an unknown solution, corresponding to a given galvanometer deflection, could be read off. Owing, however, to the fact that it was difficult to keep the amplifier balanced over a long period of time, our practice was to construct a calibration curve of two points only at the time of the colorimetric analysis of the unknown solution. With experience it was possible to locate one of these points on each side of the unknown solution.

Beer's law as expressed in equation (7) is applicable only when the light-absorbing molecules are identical. For indicators presenting one color there are no obstacles to be met because the light-absorbing molecules are all the same and colored light which is preferentially absorbed may be used. For example, the fact that picric acid solutions are yellow means that the light absorption is greater in the violet range of the spectrum. In this work a blue light of 4600 Å. was employed for picric acid solutions because of the deficiency of violet light in the source. Although with a two-color indicator there are two kinds of light-absorbing molecules, it is sometimes possible to find a wave length at which only one form of the indicator absorbs light. The yellow forms of dimethyl yellow and benzene-azodiphenylamine absorb negligible amounts of light at 5900 Å. wave length while their red forms absorb a fair amount. By using light of 5900 Å. wave length, it was possible to treat these indicators like one-color indicators. The use of light of 5750 Å. made the same procedure possible in the case of brom phenol blue (yellow-blue).

With brom cresol green it was not possible to find a wave length at which one form of the indicator absorbed no light. While there was a minimum absorption at 5800 Å. by the yellow form, it was nevertheless appreciable. In this case Beer's law has the form

$$I_{\mathrm{T}} = I_0 e^{-k_{\mathrm{A}} c_{\mathrm{A}} x} e^{-k_{\mathrm{B}} c_{\mathrm{B}} x} \qquad (9)$$

where k_{A} is the extinction coefficient and c_{A} the concentration of the acid form and k_{B} and c_{B} the extinction coefficient and concentration, respectively, of the basic form.

The procedure with brom cresol green was as follows. The extinction coefficient of the indicator wholly in its acid form, k_{A}, was obtained by measurement of the intensity of the light transmitted by solutions of concentrations c_1 and c_2. From (8) it follows that

$$k_{\mathrm{A}} = \frac{2.3}{(c_2 - c_1)x} \log \frac{I_{\mathrm{T}_1}}{I_{\mathrm{T}_2}} \qquad (10)$$

Table I shows the extinction coefficient of the acid form of brom cresol green at 5800 Å.

Table I

Extinction Coefficient of Yellow Form of Brom Cresol Green at 5800 Å.

Cell length = 10 cm.

$c \times 10^5$	$I_{\mathrm{T}} = k'$ Galv. defl.	k
0.0	20.5	
1.459	18.7	630
2.918	17.0	630
5.836	14.5	600
14.59	8.5	610
	Mean k =	617

An approximate value of the concentration of the basic form in the unknown solution was found in the customary manner. The corresponding approximate concentration of the acid form was then obtained by difference and $e^{-k_{\mathrm{A}} c_{\mathrm{A}} x}$ was computed. Dividing the galvanometer reading by $e^{-k_{\mathrm{A}} c_{\mathrm{A}} x}$ gave a corrected intensity, I'_{T}, from which a more reliable value of c_{B} was computed.

Tables II, III and IV illustrate how the calculations for *o*-toluic acid with brom cresol green were carried out.

Table II

Galvanometer Readings for *o*-Toluic Acid

Unknowns		Comparison standards		
Flask	I_{T}	Flask	I_{T}	$c_{\mathrm{IB}} \times 10^5$
35	12.5	22	10.7	2.817
		10	19.0	1.812
45	12.4	22	10.5	2.718
		10	18.7	1.812
61	12.5	22	10.6	2.718
		10	18.6	1.812

The computations from the preceding data are summarized in Table III; the columns headed "C_{IB}" give the concentration of the basic form of the indicator as read from the calibration curve.

Table III

Correction for Light Absorption by Yellow Form of Brom Cresol Green

Flask	35	45	61
$c_{\mathrm{IB}} \times 10^5$	2.47	2.45	2.46
$c_{\mathrm{IA}} \times 10^5$	1.16	1.17	1.16
$e^{-k_{\mathrm{A}} c_{\mathrm{A}} x}$	0.985	0.985	0.985
I_{T}	12.5	12.4	12.5
$I'_{\mathrm{T}} = I_{\mathrm{T}}/e^{-k_{\mathrm{A}} c_{\mathrm{A}} x}$	12.7	12.6	12.7
$c_{\mathrm{IB}} \times 10^5$	2.45	2.43	2.44
$c_{\mathrm{IA}} \times 10^5$	1.18	1.20	1.19

The concentration of the indicator was comparable to that of the buffered solution of the acid, so in calculating the acid strength constants a correction had to be made for the acid that was used to convert the indicator. That is to say, the acid was added to the basic form of the indicator and the concentration of the undissociated acid became the original acid concentration minus the concentration of the acid form of the indicator, while the concentration of the *o*-toluate ion increased the concentration of the acid form of the indicator. The values of the protolysis constant for *o*-toluic acid and the basic form of brom cresol green are given in Table IV.

TABLE IV

K_{AI_B} FOR *o*-TOLUIC ACID WITH BROM CRESOL GREEN AS INDICATOR

Flask	35	45	61
$C_{0A} \times 10^5$	22.54	45.08	67.62
$C_{0B} \times 10^5$	22.54	45.08	67.62
$C_{0I} \times 10^5$	3.625	3.625	3.625
$C_{I_B} \times 10^5$	2.45	2.43	2.44
$C_{I_A} \times 10^5$	1.18	1.20	1.19
K_{AI_B}	0.534	0.522	0.505
Mean K_{AI_B}			.520

Brom cresol green was the only indicator with which it was necessary to make a correction because of absorption of light by both acid and basic forms. With the other two-color indicators it was possible to find a wave length at which absorption by one form was negligible.

As was previously mentioned, the method of determining the protolysis of the indicators least sensitive to acids was to add a definite amount of hydrochloric acid and then measure the change in color of the indicator. This procedure was followed with dimethyl yellow, but since benzeneazodiphenylamine hydrochloride could be prepared pure, the hydrochloride was added to the solution in this case.

Preparation of Materials.—The *n*-butyl alcohol was purified by treating a commercial grade of the alcohol with sulfuric acid, distilling and refluxing over sodium hydroxide. This treatment was followed by refluxing over lime and subsequent distillation in a 17-ball Snyder column.

Lithium butylate was prepared by dissolving lithium in the pure *n*-butyl alcohol in an inert atmosphere. The solution was standardized against Bureau of Standards benzoic acid.

Lithium Chloride.—Our original plan included the study of the effect of ionic strength on the acid strength constants and a few measurements were carried out using fused lithium chloride. Difficulties with the alkalinity of the salt led us to defer that part of the work.

Acids.—Acetic acid was purified by the method of Bousfield and Lowry.[6] Monochloroacetic acid was twice crystallized from benzene, dichloroacetic acid was fractionally distilled. Picric acid was recrystallized from an aqueous solution of hydrochloric acid. The *o*-chlorobenzoic acid was purified in connection with solubility studies of Osol and Kilpatrick.[7] The other acids were Kahlbaum products which upon drying were found, by titration with standard base, to be sufficiently pure.

Bases.—The hydrochlorides of ethylamine, piperidine and aniline were dried *in vacuo* over sulfuric acid for a period of four weeks and used without further purification. Each of these was a Kahlbaum product.

Indicators.—The indicators brom cresol green and brom phenol blue were purified samples used in connection with other studies.[8] The lithium salts were prepared by adding two equivalents of lithium ethoxide to the acid dissolved in ethyl alcohol and evaporating to dryness.

The dimethylaminoazobenzene was purified by recrystallization from an alcoholic solution. The purified product melted at 117°. The benzeneazodiphenylamine was recrystallized from alcohol until the product had a melting point of 82°. The hydrochloride was prepared by the method of Witt, that is, the free base was dissolved in benzene and the hydrochloride precipitated by passing dry hydrogen chloride into the solution.[9]

Experimental Results

The experimental results are given in Tables V, VI, VII, VIII and IX, and summarized in Table

TABLE V

K_{AI_B} WITH BROM CRESOL GREEN (AT 5800 Å.)

$C_{0A} \times 10^5$	$C_{0B} \times 10^5$	$C_{I_B} \times 10^5$	$C_{I_A} \times 10^5$	K_{AI_B}
Benzoic Acid				
19.29	19.29	2.54	1.09	0.48
38.58	38.58	2.52	1.12	.47
			Mean	.475
Acetic Acid				
52.88	52.88	2.78	0.85	0.316
105.80	105.80	2.78	.85	.308
158.70	158.70	2.79	.84	.304
			Mean	.309
o-Chlorobenzoic Acid				
18.87	56.61	1.32	2.303	6.20
28.30	84.90	1.28	2.345	6.16
			Mean	6.18
Piperidinium Ion				
380.2		1.05	2.575	0.0167
570.3		0.915	2.610	.0133
380.2		1.05	2.575	.0167
			Mean	.0155
Ethylammonium Ion				
304.6		0.755	2.870	0.036
304.6		.755	2.870	.036
456.9		.660	2.985	.030
			Mean	.034

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(6) Bousfield and Lowry, *J. Chem. Soc.*, **99**, 1440 (1911).

(7) Osol and Kilpatrick, THIS JOURNAL, **55**, 4430 (1933).

(8) Chase and Kilpatrick, *ibid.*, **54**, 2284 (1932); Kilpatrick, *ibid.*, **56**, 2048 (1934).

(9) Witt, *Ber.*, **12**, 259 (1879).

X. All measurements were made at approximately 25°.

TABLE VI

K_{AI_B} WITH BROM PHENOL BLUE AS INDICATOR (MEASUREMENTS AT 5700 Å.)

$C_{0A} \times 10^5$	$C_{0B} \times 10^5$	$C_{I_B} \times 10^5$	$C_{I_A} \times 10^5$	K_{AI_B}
o-Chlorobenzoic Acid				
24.69	24.69	0.835	0.642	0.807
49.38	49.38	.82	.65	.817
			Mean	.812
m-Nitrobenzoic Acid				
37.38	37.38	0.734	0.739	1.03
56.07	56.07	.736	.737	1.04
			Mean	1.035
Monochloroacetic Acid				
31.16	93.48	0.691	0.782	3.52
62.32	186.9	.687	.786	3.51
			Mean	3.515
Cyanoacetic Acid				
37.11	148.5	0.406	1.061	10.8
74.22	297.0	.406	1.061	10.5
11.3	445.3	.406	1.061	10.6
			Mean	10.6
Dichloroacetic Acid				
38.78	97.0	0.612	0.861	3.75
58.17	145.1	.578	.895	3.92
58.17	145.1	.578	.895	3.92
			Mean	3.86

TABLE VII

K_{AI_B} WITH DIMETHYL YELLOW AS INDICATOR (MEASUREMENTS AT 5900 Å.)

$C_{0A} \times 10^4$	$C_{I_A} \times 10^4$	$C_{I_B} \times 10^4$	$K_{AI_B} \times 10^5$
Dichloroacetic Acid			
518.4	0.185	9.30	2.03
777.6	.23	9.25	2.10
		Mean	2.065
Trichloroacetic Acid			
234.4	0.35	4.39	19.7
234.4	.35	4.39	19.7
Anilinium Ion			
21.1	0.45	4.29	95,000
63.3	.785	3.96	108,000
		Mean	102,000
Solvated Hydrogen Ion			
2.482	0.49	42,500	57,000,000
4.694	.91	39,700	57,000,000

TABLE VIII

K_{AI_B} WITH BENZENE-AZODIPHENYLAMINE (MEASUREMENTS AT 5900 Å.)

$C_{0A} \times 10^4$	$C_{I_A} \times 10^5$	$C_{I_B} \times 10^5$	$K_{AI_B} \times 10^{-1}$
Solvated Hydrogen Ion			
6.798	1.42	66.56	3.12
7.554	1.77	73.77	3.09
		Mean	3.10

TABLE IX

DISSOCIATION CONSTANT OF PICRIC ACID (MEASUREMENTS AT 4600 Å.)

$C_0 \times 10^3$	$C_{B^-} \times 10^4$	$K_{A(ROH)} \times 10^5$
2.54	3.69	6.30
2.64	3.76	6.30
3.17	4.11	6.15
	Mean	6.25

TABLE X

SUMMARY OF K_{AI_B} VALUES

	K_{AI_B}
1. Brom cresol green	
1. Benzoic acid	0.475
2. Acetic acid	.390
3. *o*-Chlorobenzoic acid	.18
4. Piperidinium ion	.0155
5. Ethylammonium ion	.034
6. *o*-Toluic acid	.520
2. Brom phenol blue	
1. *o*-Chlorobenzoic acid	0.812
2. *m*-Nitrobenzoic acid	1.03
3. Monochloroacetic acid	3.515
4. Cyanoacetic acid	10.6
5. Dichloroacetic acid	3.86
3. Dimethyl yellow	
1. Dichloroacetic acid	2.07×10^{-5}
2. Trichloroacetic acid	1.97×10^{-4}
3. Anilinium ion	1.02
4. Solvated hydrogen ion	5.7×10^2
4. Benzene-azodiphenylamine	
1. Solvated hydrogen ion	3.10×10^1
Picric acid	
1. Solvated hydrogen ion	1.60×10^4

The accuracy of the results obtained depends upon the accuracy of the composition of the solutions, upon the validity of Beer's law, and upon the constant amplification of the photoelectric current. It will be noted that with the corresponding lithium salt, no deviations greater than ±2% were obtained. In other cases the deviations ran as high as 6%. To ensure constant amplification of the photoelectric current, a new calibration curve was made at the time each unknown solution was analyzed. By means of equation (6) the values of the dissociation constants were found. With dimethyl yellow as indicator K_{AI_B} was determined for four acids including the solvated hydrogen ion. From these data $K_{A(ROH)}$ was obtained for each of these acids. With $K_{A(ROH)}$ for dichloroacetic acid $K_{(ROH)I_B}$ was found from brom phenol blue and continuing in this manner $K_{A(ROH)}$ for each acid in the table was found. It is to be noted that $K_{A(ROH)}$ for an indicator is $K_{I_A(ROH)}$ which is the reciprocal of $K_{(\mathrm{ROH \cdot H^+})\mathrm{I_B}}$. The values of $K_{\mathrm{A(ROH)}}$ are summarized in Table XI; their logarithms and the logarithms of the corresponding dissociation constants in aqueous solution are also given.

TABLE XI

DISSOCIATION CONSTANTS

		n-Butyl alcohol 25° approximate		Water 25°
	Acid	$K_{\mathrm{A(ROH)}}$	Log $K_{\mathrm{A(ROH)}}$	Log $K_{\mathrm{A(H_2O)}}$
1	Brom cresol green (yellow to blue)	1.21×10^{-10}	$\overline{10}.082$	$\overline{5}.06$[a]
2	Benzoic acid	5.75×10^{-11}	$\overline{11}.760$	$\overline{5}.80$[b]
3	Acetic acid	3.74×10^{-11}	$\overline{11}.572$	$\overline{5}.24$[c]
4	*o*-Chlorobenzoic acid	7.48×10^{-10}	$\overline{10}.873$	$\overline{3}.08$[d]
5	Piperidinium ion	1.89×10^{-12}	$\overline{12}.276$	$\overline{12}.87$[e]
6	Ethylammonium ion	4.11×10^{-12}	$\overline{12}.614$	$\overline{11}.33$[e]
7	*o*-Toluic acid	6.33×10^{-11}	$\overline{11}.802$	$\overline{4}.10$[f]
8	Brom phenol blue (yellow to blue)	9.5×10^{-10}	$\overline{10}.978$	$\overline{5}.77$[g]
9	*m*-Nitrobenzoic acid	9.5×10^{-10}	$\overline{10}.978$	$\overline{4}.54$[f]
10	Monochloroacetic acid	3.25×10^{-9}	$\overline{9}.512$	$\overline{3}.14$[h]
11	Cyanoacetic acid	9.79×10^{-9}	$\overline{9}.990$	$\overline{3}.57$[f]
12	Dichloroacetic acid	3.58×10^{-8}	$\overline{8}.554$	$\overline{2}.70$[f]
13	Azobenzene dimethylammonium ion	1.71×10^{-3}	$\overline{3}.233$	$\overline{4}.71$[i]
14	Trichloroacetic acid	3.41×10^{-7}	$\overline{7}.533$	$\overline{1}.30$[j]
15	Anilinium ion	1.8×10^{-4}	$\overline{4}.254$	$\overline{5}.34$[f]
16	Benzene-azodiphenylammonium ion	3.12×10^{-2}	$\overline{2}.494$	$\overline{2}.54$[k]
17	Picric acid	6.23×10^{-5}	$\overline{5}.794$	$\overline{1}.20$[f]

[a] Kilpatrick, *Chem. Rev.*, **16,** 57 (1935). [b] Brockman and Kilpatrick, THIS JOURNAL, **56,** 1483 (1934). [c] Harned and Ehlers, *ibid.*, **55,** 652 (1933). [d] Saxton and Meier, *ibid.*, **56,** 1918 (1934). [e] Hall and Sprinkle, *ibid.*, **54,** 3478 (1932). [f] Landolt–Börnstein, "Tabellen." [g] Kilpatrick, THIS JOURNAL, **56,** 2048 (1934). [h] Wright, *ibid.*, **56,** 314 (1934). [i] Güntelberg and Schiödt, *Z. physik. Chem.*, **135,** 393 (1928). [j] Hall, *Chem. Rev.*, **8,** 191 (1931). [k] Hammett and Paul, THIS JOURNAL, **56,** 827 (1934).

The data of Table XI are summarized graphically in Fig. 2 in which log $K_{\mathrm{A(ROH)}}$ is plotted against log $K_{\mathrm{A(H_2O)}}$. Both lines in Fig. 2 are drawn with unit slope. In general we believe that these slopes may vary from unity.

For both types of acid, the logarithm of the dissociation constant in *n*-butyl alcohol is proportional to the logarithm of the dissociation constant in water. As in other cases the change in strength with change[10] in dielectric constant is in qualitative agreement with the theory.

Brönsted in a consideration of the effect of charge and medium on[11] the equilibrium constants of protolytic reactions arrives at the equation

$$\ln K_{\mathrm{A_1B_2}} = \ln K_{\mathrm{a_1}} + \ln K_{\mathrm{b_2}} + \frac{\epsilon^2}{2kTD}\left[\frac{2Z_{\mathrm{A_1}} - 1}{r_1} - \frac{2Z_{\mathrm{A_2}} - 1}{r_2}\right]$$

where $K_{\mathrm{A_1B_2}} = C_{\mathrm{B_1}}C_{\mathrm{A_2}}/C_{\mathrm{A_1}}C_{\mathrm{B_2}}$ is the equilibrium constant for the transfer of a proton from $\mathrm{A_1}$ to $\mathrm{B_2}$, $K_{\mathrm{a_1}}$ and $K_{\mathrm{b_2}}$ the constants $a_{\mathrm{H^+}}\,(a_{\mathrm{B_1}}/a_{\mathrm{A_1}})$ and $\frac{1}{a_{\mathrm{H^+}}}\frac{a_{\mathrm{A_2}}}{a_{\mathrm{B_2}}}$, respectively, ϵ the electronic charge, k the Boltzmann constant, T the absolute temperature, D the dielectric constant, Z the valence and r_1 and r_2 the effective radii of the first and second protolytes. If $\mathrm{A_2}$ is taken as the standard acid, $K_{\mathrm{A_1B_2}}$ becomes K_r in the symbols of Wynne-Jones.[12]

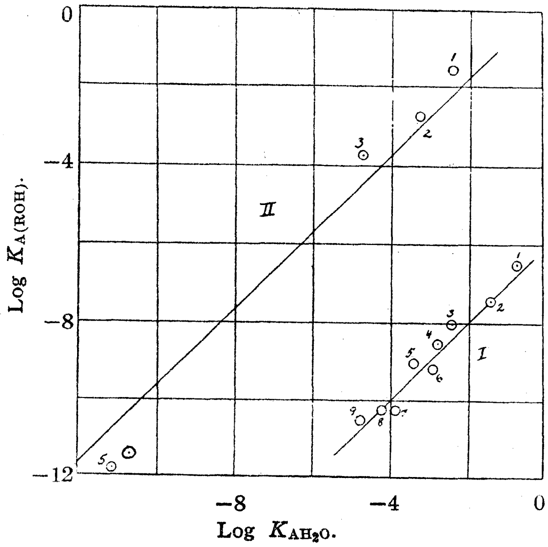

Fig. 2.—Log $K_{\mathrm{A(ROH)}}$ plotted against log $K_{\mathrm{AH_2O}}$. I. Carboxylic acids: 1, trichloroacetic acid; 2, dichloroacetic acid; 3, cyanoacetic acid; 4, monochloroacetic acid; 5, *m*-nitrobenzoic acid; 6, *o*-chlorobenzoic acid; 7, *o*-toluic acid; 8, benzoic acid; 9, acetic acid. II. Ammonium ion type acids: 1, benzene-azodiphenylammonium ion; 2, azobenzene-dimethylammonium ion; 3, anilinium ion; 4, ethylammonium ion; 5, piperidinium ion.

This author finds that if one plots the logarithm of K_r against $1/D$ for the three solvents ethyl alcohol, methyl alcohol and water the linear relationship permits an extrapolation to $D = \infty$, and an evaluation of $K_{r\infty}$ or the intrinsic acid strength. The results in the present paper are at sufficiently low ionic strengths to afford a test of the validity of this relationship.

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(10) Brönsted, Delbanco and Tovborg-Jensen, *Z. physik. Chem.*, **A169**, 361 (1934).

(11) Brönsted, *ibid.*, **A169**, 52 (1934).

(12) Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

Table XII

Log K_r for Carboxylic Acids in Various Solvents

Solvent	Water	Acetonitrile	Methyl alcohol	Ethyl alcohol	*n*-Butyl alcohol (a)	*n*-Butyl alcohol (b)	*m*-Cresol
Dielectric constant	80	37	33	25	17	17	13
Benzoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acetic acid	− .56	− .69	− .1	.0	− .19	− .05	.20
o-Toluic acid	.30	.19	...	...	.04	.02	..
m-Nitrobenzoic acid	.74	..	...	1.1	1.22	1.09	.78
o-Chlorobenzoic acid	1.28	1.09	...	1.0	1.11	1.00	..
Monochloroacetic acid	1.34	1.48	...	...	1.75	1.71	1.63
Cyanoacetic acid	1.77	..	...	...	2.23	..	2.15
Dichloroacetic acid	2.9	2.73	3.0	3.1	2.79	3.1	2.96
Trichloroacetic acid	3.50	3.88	4.3	4.4	3.77	4.1	3.88

In Table XII are listed the values of log K_r (K_r is the ratio of the dissociation constant in question to that of a benzoic acid) for a number of carboxylic acids in various solvents.

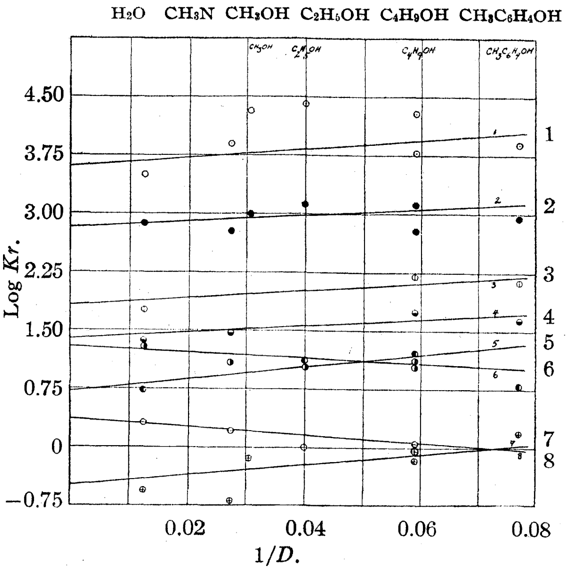

Fig. 3.—Graphic presentation of the Wynne-Jones relationship: 1, trichloroacetic acid; 2, dichloroacetic acid; 3, cyanoacetic acid; 4, monochloroacetic acid; 5, *m*-nitrobenzoic acid; 6, *o*-chlorobenzoic acid; 7, acetic acid; 8, *o*-toluic acid.

A negative value for log K_r means that the acid is weaker than benzoic acid. For aqueous solutions the K_r's were computed from the dissociation constants given in Table XI.

The values for K_r in *m*-cresol were calculated from the results of Brönsted, Delbanco and Tovborg-Jensen.[10] The source of the data for methyl and ethyl alcohol is given by Wynne-Jones. The results in acetonitrile are from the unpublished data of M. and M. L. Kilpatrick. For comparison with the results of the present study the column marked (b) under *n*-butyl alcohol gives the values from the data of Wooten and Hammett.[2] These data were obtained in the presence of 0.05 molar lithium chloride and are not strictly comparable with our data obtained at low ionic strengths. These differences are not greater than those which might be attributed to specific salt effects.

An inspection of Table XII and the graphic presentation in Fig. 3 indicates at best a qualitative agreement with the relationship of Wynne-Jones. The slopes of the lines for *o*-toluic and *o*-chlorobenzoic acid are in accord with his observations on ortho substituted acids. No correlation with the relationship was found for the ammonium type acids. Wooten and Hammett have given a different interpretation of the variation in relative strength of the carboxylic acids.

The authors would like to make due acknowledgment of a research grant made to one of us (M. K.) by the Faculty Research Committee of the University.

Summary

1. A photoelectric colorimeter has been constructed.

2. The dissociation constants of seventeen acids in *n*-butyl alcohol have been determined.

3. The results have been compared with other results in the same solvent and the acid strengths relative to benzoic acid have been compared in different solvents.

Philadelphia, Penna. Received November 30, 1936

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

The Apparent Volumes and Thermal Expansions of Certain Salts in Glycol and Methanol

BY R. E. GIBSON AND JOHN F. KINCAID

Simple theoretical considerations which give at least a rough account of many of the thermodynamic properties of electrolytes in aqueous solutions become quite inadequate when applied to describe the magnitude or the dependence on concentration of the thermal expansions of these solutions. For example, in the vicinity of 25° it is possible to obtain moderately good values of the apparent volumes or apparent compressions of salts in water at infinite dilution merely by extrapolation of data at moderate concentrations with a formula, linear in the square root of the concentration, but it seems certain that such a procedure leads to erroneous results when applied to apparent expansions. Furthermore, different salts show large individual differences even in solutions as dilute as 0.5 molal. The results of an investigation of the apparent expansions of aqueous salt solutions[1] convinced us that the peculiar properties of water play a dominant role in determining the apparent expansions of salts in this solvent and, as a step toward elucidating this behavior, we have determined the apparent volumes and apparent thermal expansions of sodium iodide, sodium bromide and lithium bromide in glycol, of lithium bromide in methanol, and the apparent volumes of potassium iodide in glycol and of sodium iodide in methanol, with the object of comparing the results with those for the same salts in aqueous solution. Water, glycol and methanol are similar chemically, all being rich in oxygen, but their compressibilities and thermal expansions are quite different. Their specific compressions to 1000 bars are 0.03940, 0.02814 and 0.10180, respectively, at 25°. The dielectric constants at 20° of water, glycol and methanol[2] are 80.37, 38.66 and 32.35, respectively.

Experimental

Measurements of the specific volumes of the solutions at 25° and of the expansions corresponding to temperature changes of 2.50° between 20 and 32.5° were made with the same apparatus[1] that was used in a study of the aqueous solutions. The temperature of the dilatometer could be held constant and measured to 0.01° and a volume change of 10^{-4} ml. could be determined readily. The specific volumes at the different temperatures were known, therefore, with a relative accuracy of approximately 2 parts in 10^6. The preparation of samples of sodium iodide,[1] sodium bromide[3] and lithium bromide[1] also has been outlined. Although our purified sample of lithium bromide gave perfectly clear solutions in water and in glycol, it produced a slightly cloudy solution in methanol. As this was eliminated by evaporating the aqueous solution from which the salt was recrystallized in a platinum rather than a Pyrex glass dish we concluded that the cloudiness was due to siliceous matter. Checks of the specific volumes of the aqueous solutions indicated that these impurities were insignificant.

An account of the preparation of *methanol* has already been given.[4] *Glycol* obtained from the Eastman Kodak Company was redistilled twice in a vacuum. The different fractions varied slightly in density, but all immediately developed a yellow color when sodium iodide was added. This color was quite intense in dilute solution but died out completely when sodium iodide sufficient to make a solution stronger than 20% was added. If the concentrated solutions were diluted, the color reappeared. When the last traces of glycolaldehyde were removed from the glycol, no coloration was produced with sodium iodide and we conclude that the peroxide of glycolaldehyde was probably responsible for the oxidation of the iodide. The reason for the disappearance of the yellow coloration in the presence of large amounts of sodium iodide is still to be investigated. It may be noted that even after standing for months in air, solutions of sodium iodide in pure glycol do not develop a yellow color. In order to obtain as accurate an estimate of the specific volume of pure glycol as possible we purified it in two different ways. The addition compound of sodium iodide with glycol was crystallized from anhydrous solution and filtered by suction from the supernatant liquor. From this solid, glycol was distilled off in a high vacuum and then redistilled. The specific volume of this sample at 25.00° was 0.90101. The commercially obtained glycol was also mixed with sodium hydroxide, distilled *in vacuo* and redistilled. This procedure freed it completely from glycolaldehyde and the specific volume of the sample was 0.90102. Three different samples treated by the same method had specific volumes of 0.90102 ml. per gram. The specific volumes of samples distilled once or twice from Eastman glycol without chemical treatment varied between 0.90095 and 0.90098. A small amount of the denser glycolaldehyde seemed to account for the discrepancies.

Results

Table I summarizes the results of the specific volume measurements. At the head of each sec-

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[1] R. E. Gibson and J. F. Kincaid, THIS JOURNAL, **59**, 25 (1937).

[2] G. Åkerlöf, *ibid.*, **54**, 4129 (1932).

[3] R. E. Gibson, *ibid.*, **57**, 284 (1935).

[4] R. E. Gibson, *ibid.*, **57**, 1551 (1935).

TABLE I

THE SPECIFIC AND APPARENT VOLUMES OF SOME SALTS IN GLYCOL AND METHANOL AT 25°

$100\ x_2$	v	ϕ_2	$(v_{\text{obsd.}} - v_{\text{calcn.}}) \times 10^5$
Sodium Iodide–Glycol			
$\phi_2 = 0.25594 + 0.08394x_2 - 0.0856x_2^2$			
0.000	0.90101		
3.352	.87949	0.2590	1
3.807	.87658	.2593	1
7.847	.85087	.2620	0
10.687	.83293	.2639	−1
15.667	.80168	.26699	0
21.523	.76521	.27004	0
30.506	.70964	.27368	3
34.879	.68263	.27489	3
39.869	.65175	.27580	0
Sodium Bromide–Glycol			
$\phi_2 = 0.26522 + 0.07303\ (x_1x_2)^{1/2}$			
1.304	0.892831	0.2731	−1
2.077	.88802	.2749	−1
4.647	.87220	.2808	1
9.361	.84348	.2863	−2
15.215	.80825	.29129	−2
19.569	.78227	.29419	0
24.983	.75011	.29696	4
Potassium Iodide–Glycol			
$\phi_2 = 0.28406 + 0.02432\ c_2^{1/2}$			
6.857	0.85918	0.2909	0
13.469	.81924	.2939	0
20.924	.77460	.2969	4
28.526	.72932	.2991	−5
Lithium Bromide–Glycol			
$\phi_2 = 0.24993 + 0.08722\ x_2^{1/2}$			
1.9962	0.888271	0.2628	1
4.069	.87524	.2676	0
8.115	.85019	.27481	0
12.360	.82430	.28034	−3
20.593	.77509	.28951	0
30.100	.71947	.29787	3
Lithium Bromide–Methanol			
0.000	1.27136		
4.033	1.22336	0.0821	
7.187	1.18679	.0952	
11.711	1.13567	.11297	
13.264	1.11835	.11806	
15.833	1.08980	.12487	
24.352	0.99772	.14779	
30.123	.93742	.16286	
35.114	.88586	.17358	
Sodium Iodide–Methanol			
$\phi_2 = 0.08542 + 0.15174\ c_2^{1/2}$			
0.000	1.27136		
7.287	1.18775	0.1242	4
14.520	1.10711	.14015	−3
22.774	1.01770	.15755	8
31.287	0.92794	.17371	5
38.209	.85682	.18642	−13

tion is written the empirical equation which best represents the data. It will be noticed that several concentration functions have been used as arguments in these equations. The choice of such functions was determined solely by which argument gave the best fit in the simplest type of equation. The last column of the table demonstrates the adequacy of the equation used.

The thermal expansion data were converted to values of $\Delta_T v$,[5] the finite changes in specific volumes for a given rise of temperature, which were expressed as quadratic functions of the temperature by a least square method.[6] Table II gives the coefficients of these equations and the deviation diagrams in Fig. 1 show how well the equations represent the observations. From the equations given in Table II the specific expansibility $(\mathrm{d}v/\mathrm{d}T)_P$ was calculated readily. The ap-

TABLE II

COEFFICIENTS IN THE QUADRATIC EQUATIONS REPRESENTING THE CHANGE IN SPECIFIC VOLUME OF THE SOLUTIONS WITH TEMPERATURE OVER THE RANGE FROM 20 TO 35°

$$\Delta_T v = A + B(t - 25) + C(t - 25)^2$$

$100\ x_2$	$A \times 10^5$	$B \times 10^5$	$C \times 10^5$
Sodium Iodide–Glycol			
0.000	0.3	57.15	0.0507
5.016	.0	53.90	.0500
10.687	.0	50.61	.0388
19.574	.0	45.67	.0354
28.578	.2	41.26	.0234
Sodium Bromide–Glycol			
5.195	0.0	53.25	0.0646
9.582	.0	50.30	.0485
14.792	.4	47.34	.0125
20.826	−.1	44.07	.0048
Lithium Bromide–Glycol			
4.069	0.0	53.09	0.0702
8.115	−.1	50.00	.0364
12.360	−.1	46.89	.0342
20.593	−.4	41.01	.0034
Lithium Bromide–Methanol			
0.000	0.0	152.54	0.3383
7.187	1.0	126.40	.1810
15.833	0.9	100.96	.1152
24.352	.1	80.42	.0366
35.114	.1	59.66	.0347

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(5) The symbols used are as follows. The subscripts 1 and 2 refer to the liquid solvent and the salt in solution, respectively; the subscripts w and s stand for pure solvent and pure solid salt, respectively. The symbol Δ_T indicates the increase with temperature of the quantity to which it is prefixed. The weight fraction is represented by x, the grams per ml. by c, the moles per liter by C, the specific volume in ml. by v, the apparent volume by ϕ, the temperature in °C. by t, the molecular weight by M. The apparent volume is defined by the relation $v = x_2\phi_2 + x_1v_w$ and the apparent expansibility at any temperature $\phi_T \equiv (\mathrm{d}\phi_2/\mathrm{d}T)_P$.

(6) H. M. Roeser, *Sci. Papers Bur. Standards*, **16**, 363 (1920).

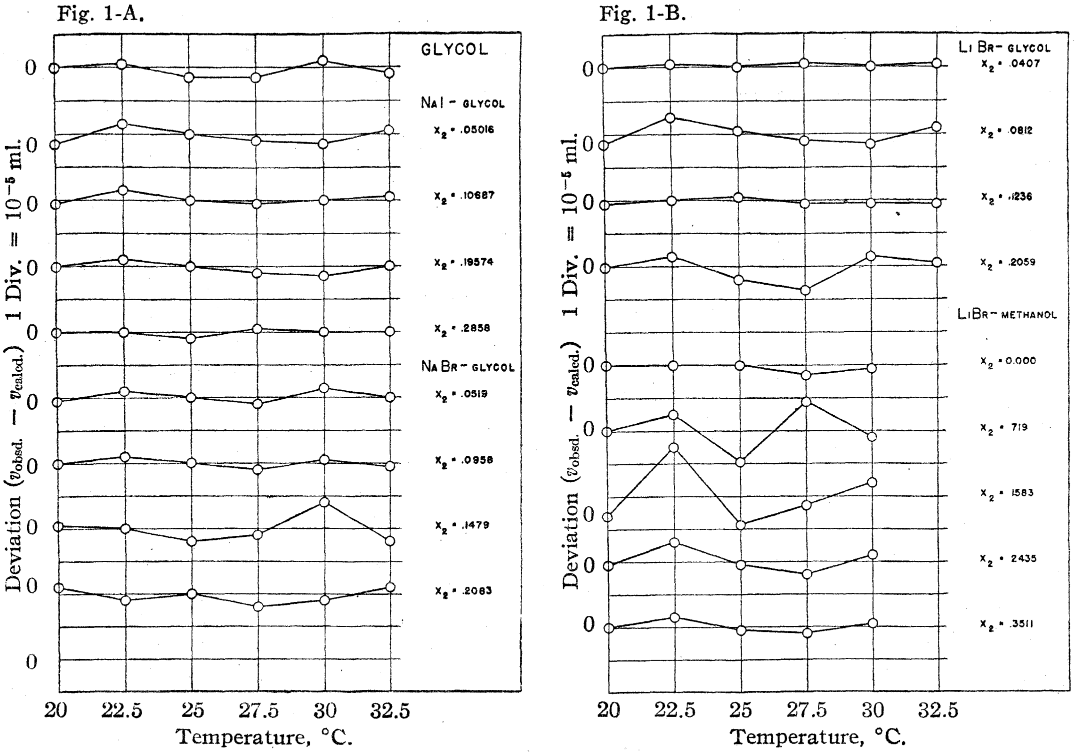
Fig. 1-A.

Fig. 1-B.

Fig. 1.—Differences between the observed specific expansions of non-aqueous solutions and those calculated by the equations in Table II.

parent expansibility was computed from the obvious relation

$$\phi_T = \frac{1}{x_2}\left[\frac{\mathrm{d}v}{\mathrm{d}T} - x_1\frac{\mathrm{d}v_w}{\mathrm{d}T}\right]$$

Discussion of Results

In Fig. 2 we have plotted $(\phi_2 - v_s)$,[7] the apparent expansion which occurs when 1 g. of salt mixes with sufficient solvent to give a solution of a given concentration, against $C_2^{1/2}$ for some of the salts in glycol, in methanol and, for purposes of comparison, in water.[1] Vosburgh, Connell and Butler[8] found that the apparent volumes of salts in dilute solutions in alcohols were linear functions of $C_2^{1/2}$ and for sodium iodide in methanol we find that this result holds in concentrated solution, but in the other cases the linear function is not adequate. It may be noted that when our results for sodium iodide solutions in methanol are extrapolated by the equation in Table I to the low concentrations investigated by Vosburgh, Connell and Butler, our specific volumes agree with theirs to within 3×10^{-5} cc.

Simple considerations lead to the conclusion that $(\phi_2 - v_s)$ should decrease algebraically with rising compressibility of the solvent for solutions of the same salt in chemically related solvents, where the forces between the solvent and the solute are roughly the same. The relative positions of the various curves in Fig. 2 are all in accord with this conclusion with one exception, namely, the curve of $(\phi_2 - v_s)$ for lithium bromide in water which lies above that of the same salt in glycol, whereas the reverse would be expected from the compressibilities of the two solvents. This phenomenon is accounted for on the now well-known hypothesis of the structure of liquid water.[9] The lithium ion in virtue of its small radius can approach close enough to a water molecule to polarize the molecule, thereby causing a strengthening of the electrostatic bonds which hold the water molecules in the less random open liquid structure (the "quartz-like" structure of Bernal and Fowler with all inference as to its exact nature removed). The effect is to cause an expansion of the water and hence to produce a smaller net contraction than if structural effects were absent. This also

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[7] Values of v_s were taken from the data of Baxter and Wallace, THIS JOURNAL, **38**, 70 (1916).

[8] W. C. Vosburgh, L. C. Connell and J. A. V. Butler, *J. Chem. Soc.*, 933 (1933).

[9] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 540 (1933); S. Katzoff, *ibid.*, **2**, 841 (1934).

accounts for the fact that the compressions of lithium salt solutions are abnormally high.[3] Such an effect is either absent or much less significant in glycol, as will be evident from the following discussion of apparent expansibilities. A reasonable extrapolation shows that in solutions of high concentration, where effects due to structural changes become less, the curve for the glycol solutions of lithium bromide should cross that for the aqueous solutions. This is seen without extrapolation in the differential effects. In Fig. 3 the partial volumes[10] of lithium bromide in glycol and in water are plotted against $C_2^{1/2}$; at low concentrations the partial volumes of lithium bromide are greater in the aqueous solutions, but when the concentration exceeds 4 moles per liter the partial volumes are greater in the glycol solutions. The apparent volumes of lithium bromide in glycol solutions also throw light on the puzzling phenomenon that, whereas the negative departures from Raoult's law in aqueous solutions indicate strong attractive forces between lithium salts and the water, the contraction on solution as measured by $(\phi_2 - v_s)$ is very small and even becomes an expansion in highly concentrated solutions. The quantity $(\phi_2 - v_l)$, where v_l is the volume of the pure liquefied solute at the temperature and pressure of the solution, should be taken as a measure of the electrostriction rather than $(\phi_2 - v_s)$ and the glycol solutions show that $(v_l - v_s)$ must be quite large for lithium bromide in comparison with other salts. A lower limit for v_l is given by the partial volume of the salt in the most concentrated glycol solution. This is at least 0.315 cc. per gram (see Fig. 3), indicating that the salt expands more than 9.1 per cent. on melting.

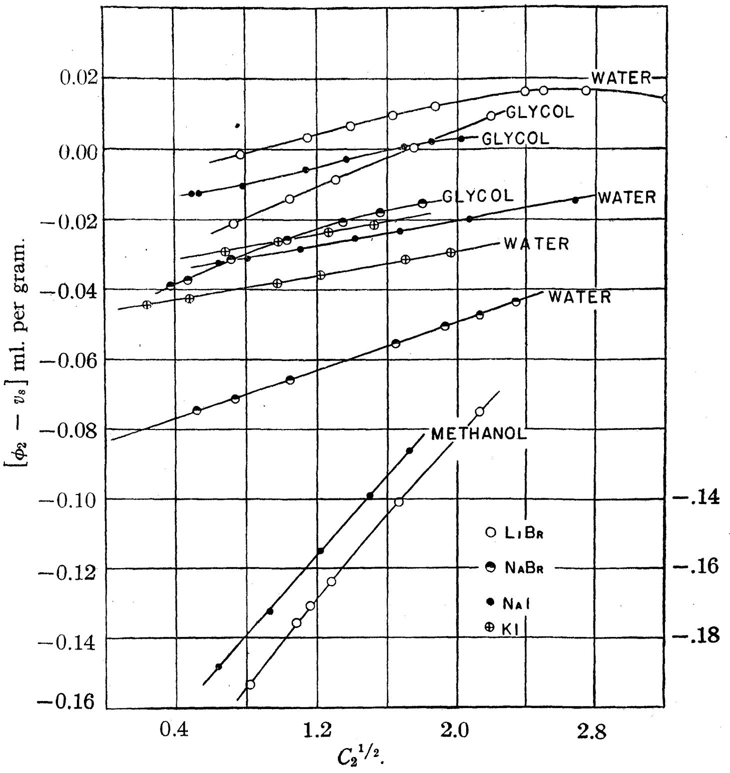

Fig. 2.—The volume changes per gram of salt accompanying the solution of salts in different solvents. The scale of ordinates on the right refers to lithium bromide in methanol.

The Apparent Thermal Expansions and Expansibilities.—In Fig. 4 the apparent molal expansibilities, $M_2\phi_T$, of the salts in different solvents are plotted against $C_2^{1/2}$. It will be seen at once that the magnitude, sign and concentration-variation of $M_2\phi_T$ for the salts in glycol and methanol are quite different from what they are in aqueous solutions. These curves for the non-aqueous solutions run in what may be regarded as a fairly normal way and by contrast bring out the abnormal behavior of similar curves for aqueous

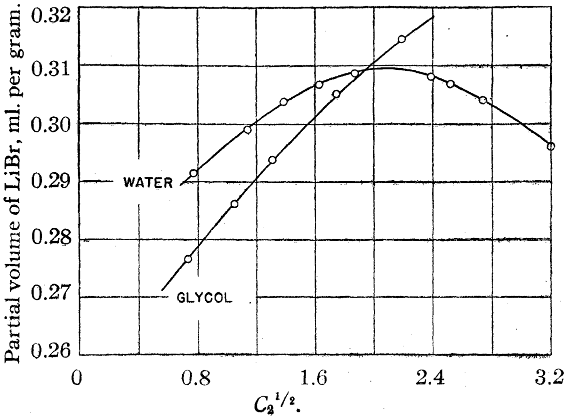

Fig. 3.—The partial volumes of lithium bromide in water and in glycol solutions as functions of the square root of the number of moles of salt per liter of solution at 25°.

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(10) The partial volumes were calculated from the apparent volumes by the formula of Adams and Gibson, This Journal, **54**, 4523 (1932). For glycol solutions $d\phi_2/dx_2$ was obtained from the equation in Table II and for aqueous solutions it was determined from tabular differences.

solutions. In general $M_2\phi_T$ is negative except in the most concentrated solutions of sodium iodide, and the slopes of the curves are positive, as would be expected from the interionic attraction theory[11] and a reasonable assumption about the effect of pressure and temperature on the dielectric constant. Data necessary for calculating the magnitudes of these slopes from the theory unfortunately are lacking.

On comparing the effect of the three salts on the expansibility of glycol we note that $M_2\phi_T$ decreases algebraically as we pass from salt to salt by an amount roughly proportional to the increase in the effective pressure of the solution, P_e,[12] as determined by compression measurements.[13] Indeed, it seems possible that, when the necessary data are at hand, ϕ_T may actually be calculated quantitatively from P_e and a knowledge of the effect of pressure on the expansion coefficient of the solvent, a thing which seems quite impossible with aqueous solutions. Furthermore, the expansion coefficient of methanol changes much more rapidly with pressure than that of glycol and it will be seen that ϕ_T for lithium bromide is much greater numerically in methanol than in glycol solutions. This again suggests that P_e may be the predominant factor in determining the expansion coefficient of these non-aqueous salt solutions.

The effective pressure hypothesis does not by any means explain the thermal expansibilities of aqueous solutions. The values of $M_2\phi_T$ are too large and, moreover, when we compare aqueous solutions of different salts we see that there is not even a qualitative relationship between the effective pressures and the thermal expansibilities. The large positive values of $M_2\phi_T$ may be explained by the assumption that salts increase the randomness of the water structure and by considering the purely mechanical effect of the volume of the dissolved ions. A detailed discussion of this cannot be given here, but it is necessary to show that the assumption made in the foregoing that lithium bromide promotes the tetrahedral arrangement of the water molecules is not incompatible with the observation that although $M_2\phi_T$ for lithium bromide in water is quite small it is, nevertheless, positive.

The observed thermal expansion of water may be regarded as the resultant of (a) an expansion due to the ordinary increase of the kinetic energy of the system as a whole, and (b) a contraction resulting from the increase in randomness as produced by a loosening up of the tetrahedral arrangement of the water molecules which is well pictured by Katzoff[9] as a departure of the O–H–O angles from 180°. The magnitude of contraction (b) depends on the amount of randomness introduced by a given rise of temperature and on the amount of excess volume which the tetrahedral structure introduces into the system.

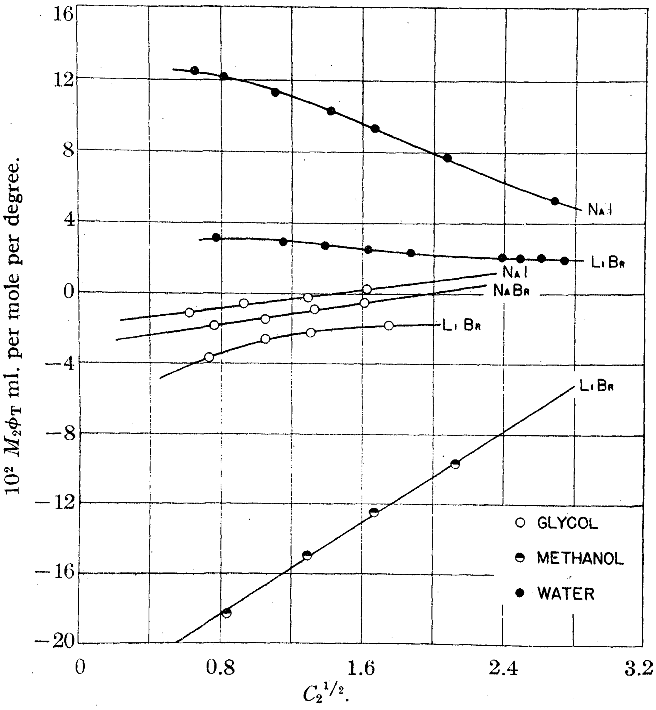

Fig. 4.—The apparent molal expansibilities at 25° of salts in different solvents as functions of the square root of the number of moles of salt per liter of solution.

Because of its polarizing power, the lithium ion, we have supposed, increases the strength of those bonds which hold the water molecules in the tetrahedral arrangement. We should, therefore, expect that a given rise of temperature would introduce less randomness into water in lithium bromide solution than in pure water and hence that contraction (b) would be diminished. This would lead to an apparent expansibility of the water in the solution larger than that of pure water and hence a positive value of $M_2\phi_T$, as is observed.

The specific volume of water is 84% greater than if the molecules of radius 1.4 Å. were packed

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[11] F. T. Gucker, Jr., THIS JOURNAL, **56**, 1017 (1934).

[12] R. E. Gibson, *ibid.*, **56**, 13 (1934).

[13] Unpublished results obtained in this Laboratory.

closely together.[9] The excess volume introduced by the tetrahedral arrangement is therefore approximately 45% of the total volume. The expansion coefficient of water at 25° is 25.7×10^{-5} ml. per gram per degree. If it behaved as a normal liquid it would have an expansion coefficient of approximately 85×10^{-5} ml. per gram per degree. This difference may be accounted for if we assume that a rise of one degree introduces a randomness which corresponds to a loss of about 0.1% of the excess volume, a very reasonable amount.

Summary

We have measured the specific volumes at 25° and the expansion coefficients in the neighborhood of this temperature of solutions of some salts in methanol and glycol. A comparison of the apparent and partial volumes of lithium bromide in water, glycol and methanol gives strong evidence that this salt influences the structure of water by promoting the tetrahedral arrangement of the molecules.

Unlike the same quantities for salts in aqueous solution, the apparent molal expansibilities of the salts in glycol and methanol are negative and increase with the concentration of salt, thereby agreeing qualitatively with the predictions of the interionic attraction theory and the effective pressure hypothesis. A comparison of the behavior of the salts in water on the one hand and in glycol and methanol on the other indicates that the structural changes in water play a predominant role in determining the thermal expansions of aqueous solutions.

WASHINGTON, D. C. RECEIVED DECEMBER 26, 1936

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Rate of Reaction of Magnesium with Acids in Ethyl Alcohol[1,2]

BY MARTIN SCLAR[3] AND MARTIN KILPATRICK

The rate of reaction of metals with acids in aqueous solution has been the subject of many investigations. A summary of the work up to 1929 has been given by Centnerszwer.[4] In non-aqueous solvents two quantitative studies have appeared. Zecchini[5] measured the rates of reaction of zinc with hydrogen chloride in water, ethyl alcohol, methyl alcohol and acetone. Brönsted and Kane[6] sought to show that sodium amalgam reacted with molecules of carboxylic acids in benzene, and that the rate of the reaction increased with the ease with which the acid gave up its proton. In addition, several partially quantitative observations have been made, especially by Kahlenberg and his co-workers in connection with their criticism of the Arrhenius theory of electrolytic dissociation. Smith[7] gives a summary of this work. Additional investigations are desirable because comparison of the results in aqueous and non-aqueous solutions may lead to a better understanding of the problem.

In the present work ethyl alcohol was selected as the solvent and magnesium as the metal for the general study. After describing the procedure and some orientating experiments, we shall proceed to demonstrate that magnesium can displace hydrogen from the molecules of ethyl alcohol without the intermediate formation of solvated proton. We shall also show that this reaction predominates when magnesium dissolves in alcoholic solutions of acids. It will be seen that the observed rate of this reaction shows great variations. Experiments with solutions of acids containing chloride ion, organic chlorine compounds and small amounts of water, respectively, will be described, which indicate that the variations in the observed rates probably are due to differences in the amount of metal surface available for reaction. The results of experiments to determine the effect of temperature and the rate at which the magnesium cylinder is rotated will then be presented. Finally some miscellaneous experiments will be described.

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(1) Abstracted from the dissertation of Martin Sclar presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1935.

(2) An abstract of this paper was presented at the eighty-ninth meeting of the American Chemical Society held at New York, April, 1935.

(3) George Leib Harrison Fellow in Chemistry, 1934–1935.

(4) Centnerszwer, *Z. physik. Chem.*, **141A**, 297 (1929).

(5) Zecchini, *Gazz. chim. ital.*, **27**, 466 (1897).

(6) Brönsted and Kane, THIS JOURNAL, **53**, 3624 (1931).

(7) Smith, "The Effects of Moisture on Chemical and Physical Changes," Longmans, Green and Co., London, 1929, Chap. 14.

Experimental

1.—The experimental procedure is essentially a modification and improvement of that of Kilpatrick and Rushton.[8] Figure 1 is a diagram of the apparatus. The reaction vessel was located in an air thermostat regulated at 30 ± 0.05°. The cylinder of magnesium was rotated at 980 r. p. m. by a small synchronous motor. Other speeds were obtained by the use of gears. A piece of Bakelite was inserted between the steel shaft and the magnesium, and the latter was completely immersed. The solution was added from a fast delivering 50-cc. pipet to the reaction vessel through the side-arm extending through the top of the thermostat. The gas evolved was collected over anhydrous ethyl alcohol in a water-jacketed double-armed buret.

The ethyl alcohol was dried by the method of Bjerrum and Lund.[9] Density measurements on various batches showed that the water content did not exceed 0.025%. Dried nitrogen was bubbled through the alcohol to remove oxygen.

The solutions of hydrogen chloride were freshly prepared, and precautions were taken to exclude moisture. The carboxylic acids were purified where necessary. All acid solutions were diluted to the desired concentration and standardized against 0.1 *M* sodium hydroxide one-half hour before use. Solutions of lithium chloride were prepared from Kahlbaum fused lithium chloride, which was found to contain a negligibly small amount of alkali.

Kahlbaum magnesium was used in the form of cylinders about 0.9 cm. in diameter and 5.5 cm. in length. Zinc cylinders of the same dimensions were cast in vacuum from a supply of very pure zinc.[10] Before use a skin was removed from each cylinder by turning on a lathe. Then the metal was washed with carbon tetrachloride and ethyl alcohol, polished with emery paper and wiped with a dry cloth.

Each experiment was carried out in duplicate, and at least 3 runs were made when the reproducibility was unsatisfactory. The reproducibility varied with the acid used, hydrochloric and the chloro acids yielding much better results than acetic acid. Different batches of alcohol gave the same results. It made no difference whether or not the magnesium was polished with emery paper. Table I shows the reproducibility of the results with hydrochloric and chloroacetic acids.

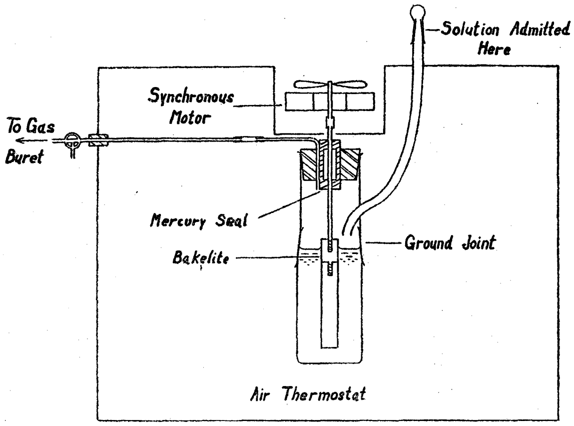

Fig. 1.—Apparatus.

2.—Whitby[11] and Kilpatrick and Rushton[8] found that no oxygen was consumed when magnesium dissolved in aqueous solutions of sodium chloride and acids, respectively. When ethyl alcohol is the solvent, however, considerable quantities of hydrogen are lost as a result of its combination with oxygen. This can be seen from the data in the last three rows of Table II. The difference in the results in water and in alcohol may be due to the fact that oxygen is 8.6 times more soluble in alcohol than in water[12] at 76 cm. of oxygen. However, when oxygen is removed from both the alcohol and the reaction vessel, the hydrogen evolved, the magnesium dissolved and the acid consumed are equivalent to within a few per cent. The results of some of the experiments which were carried out to determine this are given in Table II. Therefore, unless otherwise noted, oxygen was excluded in the experiments. Additional reasons for excluding oxygen were: first, in some cases oxygen increases the rate of the reaction in the initial stages, and, second, the formation of water inhibits the reaction.

TABLE I

REPRODUCIBILITY OF THE DISSOLUTION OF MAGNESIUM IN ACIDS AT 30°

0.065 *M* Hydrochloric Acid[a,b]

Minutes				
2	5	11	18	25
Equivalents hydrogen evolved × 10^4/cm.^{2}				
0.258	0.825	1.47	1.98	2.36
.255	.811	1.47	1.98	2.35
.222	.818	1.51	1.98	2.37
.297	.795	1.46	1.96	2.34

[a] The first and last two experiments, respectively, were carried out with different batches of alcohol. [b] In the last experiment the metal was not polished with emery.

0.059 *M* Monochloroacetic Acid

5	12	18	25	32
Equivalents hydrogen evolved × 10^4/cm.^{2}				
0.122	0.480	0.965	1.44	1.93
.122	.464	.952	1.42	1.85

The equivalence of the gas evolved, metal dissolved and acid consumed indicated that the chlorine-substituted acids which were used were only

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(8) Kilpatrick and Rushton, *J. Phys. Chem.*, **38**, 269 (1934).

(9) Bjerrum and Lund, *Ber.*, **64B**, 210 (1931).

(10) The authors take this opportunity to thank the New Jersey Zinc Co. for the zinc.

(11) Whitby, *Trans. Faraday Soc.*, **28**, 474 (1932).

(12) Calculated from data in the "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VIII, 1928, pp. 257 and 262.

TABLE II

EQUIVALENCE OF GAS EVOLVED, METAL DISSOLVED AND ACID CONSUMED

Acid and initial molarity[a]	Hydrogen, cc. at N. T. P. Expected from wt. loss	Expected from acid consumed	Obtained
0.148 acetic	81.0	84.5	82.0
.122 chloroacetic	84.5	85.0	85.0
.117 α-chloropropionic		95.3[b]	96.5
.119 *o*-chlorobenzoic	80.5	82.6	83.8
.117 dichloroacetic	87.5	85.3	84.9
.112 dichloroacetic	123[b]		126[c]
.0646 hydrochloric	34.4	35.8	36.4
.0512 hydrochloric[d]	26.4		20.4
.144 acetic[d]	78.5		70.3
.0588 chloroacetic[d]		30.1	22.9

[a] Salts present not noted. [b] Solution alkaline at end of experiment. [c] Experiment at 50°. [d] Oxygen not excluded.

slightly reduced. Lund[13] heated 1 g. of magnesium with 30 cc. of alcohol containing 1 cc. of carbon tetrachloride until the metal dissolved completely, and found that the amount of chloride ion in the resultant solution corresponded to only 8% of the total. In that experiment the volume of hydrogen evolved was about 1000 cc. or 10 times the volume evolved in our experiments. In the latter, therefore, where the maximum concentration of chlorine compound was about one-half of that used by Lund and the maximum temperature 50°, the amount of reduction was probably slight. Kilpatrick and Rushton[8] working with aqueous solutions found that the chloro acids used by them were not reduced. However, Tarle,[14] Bodforss and Kajmer[15] and Dunning and Fletcher,[16] the latter working with sodium and lithium amalgams, observed reduction.

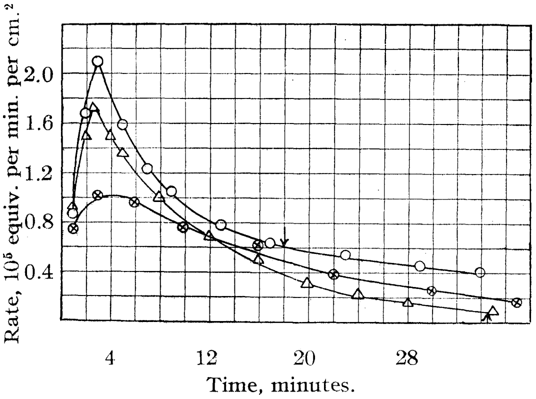

Fig. 2.—Effect of water on the reaction of magnesium with 0.064 *M* hydrochloric acid. The arrow indicates when all the acid has been consumed. The circles, triangles and crossed circles show the rates obtained with solutions which were 0.011, 0.050 and 0.102 *M* in water, respectively.

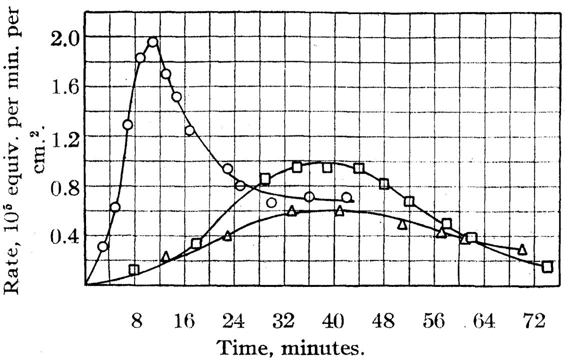

Fig. 3.—Effect of water on the reaction of magnesium with 0.12 *M* chloroacetic acid. The circles, squares and triangles show the rates obtained with solutions which were 0.011, 0.024 and 0.05 *M* in water, respectively.

3.—Data for some typical experiments are presented graphically in Figs. 2, 3 and 4. From them it may be observed that, in contrast to the behavior in aqueous solutions of acids, induction periods are observed in alcohol. After the induction period the reaction rate decreases, and the magnesium continues to liberate hydrogen from the alcohol after a volume of hydrogen equivalent to the acid originally present has been evolved, despite the fact that magnesium does not react with pure boiling ethyl alcohol. We have been

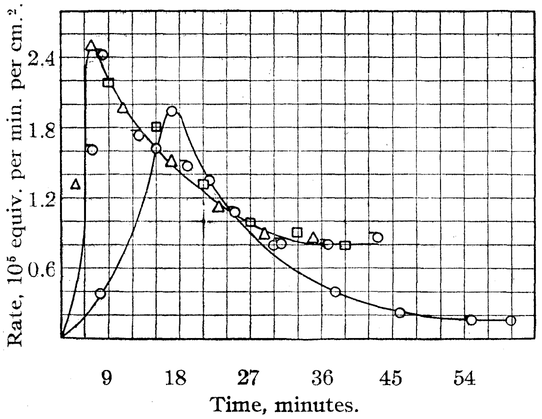

Fig. 4.—The effect of lithium chloride on the solution of magnesium in 0.12 *M* acetic acid. The circles, triangles, squares and tailed-circles show the rates for solutions which were 0.0, 0.025, 0.05 and 0.10 *M* in lithium chloride, respectively.

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(13) Lund, *Ber.*, **67B**, 935 (1934).

(14) Tarle, Dissertation, Leipzig, 1911.

(15) Bodforss and Kajmer, *Z. physik. Chem.*, **A171**, 190 (1934).

(16) Dunning and Fletcher, unpublished results, this Laboratory.

unable to fit a reaction rate equation to any portion of the reaction for experiments of this type. Since the "alcohol reaction" after the "equivalence point" is not complicated by the presence of acid, we shall deal with it first.

The velocity of this reaction is too great to be accounted for on the basis of the number of collisions of hydrogen ion, $C_2H_5OH_2^+$, with the surface of the metal. Therefore, alcohol molecules must react with magnesium. A simple calculation will demonstrate this.

From Table X, in which some data on the effects of stirring are presented, it can be seen that at 30° a reaction velocity as high as 0.705×10^{-5} equivalent per min. per sq. cm. has been observed in 0.05 *M* magnesium ethylate. This rate would require $0.705 \times 10^{-5} \times 6.06 \times 10^{23} = 4.27 \times 10^{18}$ collisions of hydrogen ion per minute with one sq. cm. of the magnesium cylinder, if every colliding ion gave up its proton. Now, the ionic product of ethyl alcohol is[17] about 10^{-20}, so that the concentration of solvated proton in 0.05 *M* ethylate is 10^{-22} mole per cc. For this concentration of solvated proton, the number[18] of collisions of the protons per minute with one sq. cm. of the magnesium cylinder is 3.36×10^7. Therefore, the ratio of the number of collisions which occur to the minimum number required is 7.87×10^{-12}, or collisions of hydrogen ion with the surface of the metal could account for only $7.87 \times 10^{-10}\%$ of the observed reaction. The answer for a similar calculation, which was made for an observed reaction velocity of 2.72×10^{-5} equivalent per min. per sq. cm. at the equivalence point, is 0.20%. These calculations constitute a definite proof that metals can displace hydrogen from the molecules of acids without the intermediate formation of solvated proton.

4.—We shall now try to determine what portion of the reaction rates which are observed when acid is present is due to the reaction of the alcohol molecules with magnesium. In order to do this it will be necessary to compare the reaction rates obtained with magnesium and zinc, respectively, with hydrochloric acid.

TABLE III

EXPERIMENTS AT 30° WITH MAGNESIUM AND HYDROCHLORIC ACID

N_i = initial molarity of acid. N_m = molarity of acid at point of maximum rate. *M* = maximum rate of reaction. *R* = equivalents per sq. cm. reacted during induction period. *T* = minutes elapsed during induction period. *F* = equivalents of magnesium dissolved per min. per sq. cm. at the equivalence point.

N_i, mole/l.	N_m, mole/l.	*M*, 10^5 equiv./min./cm.^{2}	*R*, 10^5 equiv. per cm.^{2}	*T*, min.	*F*, 10^5 equiv./min./cm.^{2}
0.0285	0.0191	0.960	2.75	4.5	0.371
.0407	.0288	1.25	3.20	3.8	.312
.0654	.0534	2.21	3.68	2.5	.598
.0969	.0844	3.16	4.02	1.5	.645
.101	.0828	3.22	5.35	2.3	.625
.112	.0975	3.78	4.31	1.8	.705

Detailed data for the experiments with magnesium are to be found in Table III. As previously stated we have been unable to fit a reaction rate law to individual experiments of this type. However, we have found that a fairly straight line is obtained on plotting the maximum rate of reaction, that is, the rate at the end of the induction period, *versus* the concentration of acid at the time of maximum rate. The plots for hydrochloric and the other acids are given in Fig. 5. From these plots we can find the maximum rate of reaction for any corresponding concentration of acid.

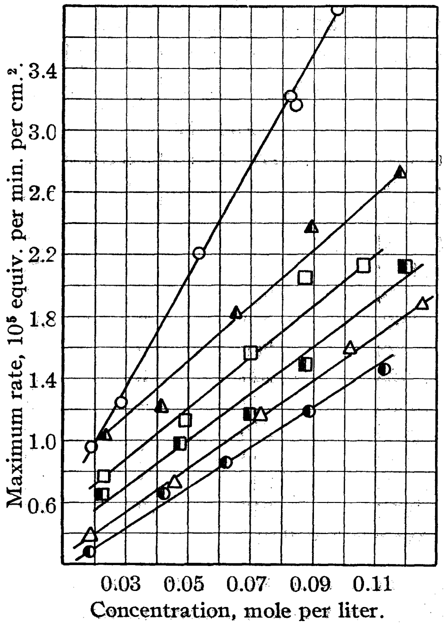

Fig. 5.—Maximum rate of reaction *versus* the concentration of acid at the time of maximum rate. Circles, hydrochloric acid. Shaded triangles, chloroacetic (up 0.4). Squares, acetic (up 0.4). Shaded squares, dichloroacetic (down 0.1). Triangles, *o*-chlorobenzoic (down 0.1). Shaded circles, α-chloropropionic (down 0.5). In parentheses is given the number of units the line is displaced. A point has been omitted for acetic acid at concentration = 0.074, rate = 1.04.

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(17) MacFarlane and Hartley, *Phil. Mag.*, **13**, 425 (1932).

(18) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, Oxford, 1933, p. 281.

The results of the experiments with zinc and alcoholic hydrochloric acid are summarized in Table IV. We have found that zinc dissolves in alcoholic hydrochloric acid in accordance with the unimolecular reaction rate law. The zinc reacts only with hydrogen ion, $C_2H_5OH_2^+$. The average unimolecular velocity constant, $k = (2.3\ V/St) \log a/(a - x)$, is 0.217 cm. per min. V is the volume of the solution in cc., S the area of the metal cylinder in sq. cm. and t the minutes elapsed since the start of the experiment. a is the concentration of acid at the start of the experiment and $a - x$ the concentration at the time t.

Sometimes a short induction period was observed, and the reaction velocity decreased too rapidly at the end of the experiment for the reaction rate law to be obeyed. The extent of these deviations is also given in Table IV. The addition of lithium nitrate as a depolarizer did not speed up the reaction. When lithium nitrate was present very little hydrogen was evolved, which shows that it was an efficient depolarizer.

TABLE IV

EXPERIMENTS AT 30° WITH ZINC AND HYDROCHLORIC ACID

Molarity of acid, mole/l.	k, cm./min.	Induction period, min.	% law obeyed
0.1203	0.213	0	91
.1153	.195	2	88
.1159	.281	0	94
.1140	.231	0	90
.1123	.200	0	81
.1128	.224	6	88
.0635	.157	4	78
.0636	.210	1	75
.0615	.214	1	46
.0288	.245	4	94
.0296	.213	10	37
Average k = 0.217			

King and his co-workers[19,20] have found that magnesium and zinc dissolve in aqueous hydrochloric acid with very nearly the same velocity. If the reaction of the magnesium were with the $C_2H_5OH_2^+$ alone, we should expect the same result for the two metals with alcoholic hydrochloric acid. When different solids dissolve in identical solutions with the same velocity, it is generally conceded that the rates of the reactions are governed by the speed with which the dissolved reactant is transported to the surface of the solid. Therefore, a comparison of the results obtained with magnesium and zinc, respectively, and hydrochloric acid should enable us to determine what portion of the maximum reaction rate is due to the reaction of the magnesium with alcohol.

Using the velocity constant $k = 0.217$ cm. per min. for the dissolution of zinc in alcoholic hydrochloric acid, reaction rates have been calculated for three concentrations of acid, which would also be correct for magnesium if it reacted only with the acid. These rates are compared in Table V with those taken from the plots of maximum rate of reaction *versus* the concentration of acid at the time of maximum rate in Fig. 5. From the data in the table it would appear that ethylate ion was being generated at the surface of the metal about as fast as hydrogen ion was scheduled to arrive. On this basis most of the acid would be neutralized before it reached the magnesium. Then to account for the observed rates we would have to raise the estimate of the portion of the reaction due to the reaction of the metal with the alcohol molecules considerably. The ethylate would then be produced much more rapidly than the hydrogen ion was scheduled to arrive. This would mean that practically no hydrogen ion reaches the surface, so that the observed reaction rate must be almost entirely an alcohol reaction and the region immediately adjacent to the surface of the metal must be alkaline. The same picture applies to the carboxylic acids. In brief, the alcohol reaction predominates, and the rapid production of ethylate ion prevents any reaction with acids other than the solvent.

TABLE V

COMPARISON OF THE RATES OF SOLUTION OF MAGNESIUM AND ZINC IN HYDROCHLORIC ACID AT 30°

N_m, mole/liter	M (for Mg) 10^5 equiv./min./cm.^{2}	Rate for Zn (Z) 10^5 equiv./min./cm.^{2}	M − Z, 10^5 equiv./min./cm.^{2}	(M − Z)/M
0.03	1.35	0.65	0.70	0.52
.06	2.44	1.30	1.14	.47
.09	3.52	1.95	1.57	.45

5.—It is apparent from the tables and graphs that the observed rate of the reaction after the induction period varies considerably. Now if the reaction is always one of magnesium with alcohol, the concentration of which is practically constant, some explanation must be found for this variation. The results of experiments with solutions of acids containing chloride ion and small amounts of water, respectively, indicate that the variation is due to differences in the amount of metal surface available for reaction. Small traces of water retard the reaction and chloride ion speeds it up.

The water content of the dehydrated alcohol

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(19) King and Braverman, THIS JOURNAL, **54**, 4774 (1932).

(20) King, *ibid.*, **57**, 828 (1935).

was 0.025%, corresponding to a molarity of 0.011. The effect of adding small amounts of water to solutions of hydrochloric and chloroacetic acids made from the dehydrated alcohol can be seen from Figs. 2 and 3, respectively. From the plots of rate *versus* time we note that the addition of water depresses the rate. Seligman and Williams[21] and Zecchini[5] observed a similar result for the solution of aluminum in phenol and glacial acetic acid and zinc in alcoholic hydrochloric acid, respectively. The inhibitory effect of water is usually attributed to the formation of a difficultly soluble coating of hydroxide on the surface of the metal. This coating is supposed to result from the reaction of the metal with the water. That we can vary the rate of reaction by causing a portion of the surface of the metal to become covered with a coating during the course of an experiment indicates that the original variations in rate are due to differences in the amount of surface available for reaction. It also shows that the amount of clean surface varies in the same experiment.

It should be pointed out that the addition of water to the dehydrated alcohol did not destroy the reproducibility of the experiments with hydrochloric acid, but did destroy it for the experiments with chloroacetic acid. In the latter case, therefore, the faster of two duplicate experiments was used for comparison.

6.—From Fig. 4 it may be seen that the addition of lithium chloride to acetic acid solutions speeds up the reaction during the induction period and at the equivalence point. The fact that chloride ion hastens corrosion has been observed by many investigators, and the effect is generally ascribed to the ability of that ion to penetrate coatings. The results of these experiments, in conjunction with the fact that induction periods were observed, are evidence, therefore, that the magnesium cylinders contain an invisible coating before being placed in the acid solutions. This coating must be removed before the alcohol can react with the metal, and the magnitude of the observed reaction depends on the extent to which the coating is removed. From Fig. 4 it also may be seen that the effects due to chloride ion were independent of its concentration between 0.025 and 0.1 M.

7.—With certain organic chlorine compounds results were obtained which were similar to those observed with chloride ion. Thus from Table VI it may be seen that solutions of acetic acid which are 0.12 M in ethyl dichloroacetate, chloroform or carbon tetrachloride dissolve magnesium more rapidly than solutions of acetic acid alone. This happens despite the fact that magnesium does not dissolve in 0.12 M solutions of these substances in alcohol at 30°. From the data it is also seen that the compound with the greatest number of chlorine atoms in the molecule speeds up the reaction most. The effects were found to decrease with the concentration of chlorine compound, but in no regular manner. Similar results were observed in a few experiments with *o*-toluic and phenylacetic acids. They could not be used alone to any considerable extent, because with them the metal bore scattered deep pits at the conclusion of an experiment, and because the reproducibility was exceedingly poor. This pitting and poor reproducibility, which were observed with acetic acid alone to a smaller extent, are further evidence that the surface of the metal is not entirely available for reaction.

TABLE VI

THE EFFECT OF CHLORINE COMPOUNDS ON THE RATE OF SOLUTION OF MAGNESIUM IN 0.125 M ACETIC ACID

Concentration of chlorine compound = 0.12 M

Chlorine compd.	N_m, mole/liter	M, 10^5 equiv./min./cm.^{2}	M/N_m	F, 10^5 equiv./min./cm.^{2}	Induction, pd., min.
None	0.0699	1.11	15.9	0.15	29.0
Ethyl dichloroacetate	.1107	3.21	29.0	1.35	2.5
Chloroform	.0947	3.26	34.4	1.55	5.5
Carbon tetrachloride	.101	4.30	42.6	1.69	3.5

TABLE VII

EXPERIMENTS AT 30° WITH MAGNESIUM AND CHLOROACETIC ACID

N_i, mole/liter	N_m, mole/liter	M, 10^5 equiv./min./cm.^{2}	R, 10^5 equiv. per cm.^{2}	T, min.	F, 10^5 equiv./min./cm.^{2}
0.0297	0.0232	0.635	2.00	5.5	0.368
.0588	.0419	.823	5.14	12.5	.594
.0909	.0654	1.42	7.75	9.5	.776
.121	.0894	1.97	9.25	9.5	.629
.150	.118	2.32	9.55	9.3	.689

From the similarity of the results with chloride ion and the chlorine compounds it appears that the latter also clean the surface of the metal. We cannot say how they do this. However, it is not probable that the similarity is due either to the formation of chloride ion resulting from the reduction of the chlorine compounds or to those compounds acting as depolarizers. We have al-

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(21) Seligman and Williams, *J. Soc. Chem. Ind.*, **35**, 188 (1916); **37**, 159 (1918).

ready shown that the amount of reduction is very small.

TABLE VIII

COMPARISON OF THE MAXIMUM RATES OF SOLUTION AT 30° OF MAGNESIUM IN DIFFERENT ACIDS[a]

N_m, mole/liter	Maximum rates (M) in 10^5 equivalents per min. per cm.^{2} Acetic	Chloro-acetic	α-Chloro-propionic	*o*-Chloro-benzoic	Dichloro-acetic
0.03	0.50	0.74	0.94	0.62	0.78
.06	1.00	1.28	1.34	1.06	1.24
.09	1.49	1.82	1.73	1.50	1.71

[a] For hydrochloric acid see Table V.

The curves in Fig. 5 enable one to obtain the maximum rates of reaction for the same concentration of different acids. (The data used to construct the curve for chloroacetic acid are contained in Table VII.) Maximum rates obtained in this manner are compared in Table VIII. With the exception of *o*-chlorobenzoic acid, the rates for the chloro acids are greater than those for acetic acid. While we should have predicted this from the results of the experiments with acetic acid and the chlorine compounds, we should also have expected greater rates with dichloroacetic acid than with monochloroacetic and α-chloropropionic acids. However, the rates at 30° of the alcohol reaction at the equivalence point, which were obtained with 0.12 M solutions of the five carboxylic acids, may be divided into three distinct groups, according to the number of chlorine atoms to the molecule. For the acids in the order in which they are given in Table VIII the rates are 0.145, 0.660, 0.885, 0.715 and 1.13×10^{-5} equivalents per min. per sq. cm., respectively.

8.—The rate at which the magnesium cylinder rotates and the temperature also affect the maximum rates of reaction and the alcohol reaction. The results of experiments to determine the extent of these influences are presented in Tables IX to XII.

TABLE IX

INFLUENCE OF STIRRING AT 30° ON THE MAXIMUM RATES OF SOLUTION OF MAGNESIUM IN ACIDS

Acid	N_m, mole/liter	Max. rate in 10^5 equiv./min./cm.^{2} 520 r. p. m.	980 r. p. m.	1980 r. p. m.
Hydrochloric	0.06	1.45	2.42	3.23
Hydrochloric	.09	2.23	3.50	4.58
Chloroacetic	.06	1.06	1.31	1.73
Chloroacetic	.09	1.51	1.87	2.38

TABLE X

INFLUENCE OF STIRRING ON THE ALCOHOL REACTION AT 30° REACTION STARTED WITH 0.115 M DICHLOROACETIC ACID

R. p. m.	Rate of alc. react. in 10^5 equiv./min./cm.^{2} At 0.0	0.025	0.05 M magnesium ethylate
520	0.976	0.653	0.452
980	1.23	.932	.561
1980	2.72	1.72	.705

TABLE XI

INFLUENCE OF TEMPERATURE ON THE MAXIMUM RATES OF SOLUTION OF MAGNESIUM IN ACIDS

N_m, mole/liter	Max. rate (M) in 10^5 equiv./min./cm.^{2} 30°	40°	50°	M_{40}/M_{30}	M_{50}/M_{40}
		Hydrochloric Acid			
0.03	1.35	1.23	2.05	0.9	1.7
.09	3.50	3.04	3.82	.9	1.3
		Chloroacetic Acid			
0.03	0.757	1.18	1.60	1.6	1.4
.09	1.87	2.70	3.15	1.4	1.2

TABLE XII

INFLUENCE OF TEMPERATURE ON THE ALCOHOL REACTION[a] REACTION STARTED WITH 0.115 M ACID

Average rate (A) in 10^4 equiv./min./cm.^{2}

Acid	Average rate (A) in 10^5 equiv./min./cm.^{2} 30°	40°	50°	A_{40}/A_{30}	A_{50}/A_{40}
	From 0.0 to 0.025 M magnesium ethylate				
Dichloroacetic	1.11	1.34	1.69	1.2	1.3
α-Chloropropionic	0.88	1.36	1.76	1.5	1.3
	From 0.025 to 0.05 M magnesium ethylate				
Dichloroacetic	0.73	0.86	1.02	1.2	1.2
α-Chloropropionic acid	.622	.88	1.06	1.4	1.2

[a] Approximate solubility of magnesium ethylate = 0.1 M at 30°.

The maximum rates were taken from plots of maximum rate *versus* concentration of acid at the time of maximum rate. They are given for only two concentrations of acid because the fractional changes did not differ to any considerable extent for the other concentrations. The stirring effects are not sufficiently[20,22] great and the temperature effects not sufficiently small to indicate that the observed rates of reaction are controlled solely by diffusion processes. However, the diffusion of solutes must be a contributing factor. Because the reproducibility of the experiments at 40 and 50° was not good, and it was difficult to draw a curve through the points obtained on plotting maximum rate *versus* concentration of acid at the time of maximum rate, too much weight should not be given to the negative temperature coefficients for hydrochloric acid in Table XI. Moreover, at 40 and 50° it was difficult to select the points of maximum reaction for the higher concentrations of acid, because the induction periods were exceedingly short and the reaction velocities inconveniently rapid.

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(22) Roller, *J. Phys. Chem.*, **39**, 221 (1935).

In connection with the results for the alcohol reaction, we have found that the solubility of magnesium ethylate is approximately 0.1 *M* at 30°. Consequently the progressive decrease in the reaction rate after the equivalence point could not be due to the insolubility of that substance.

9.—A description of some miscellaneous experiments concludes the presentation of the experimental results.

The presence of oxygen in the alcohol and reaction vessel was found to affect the rates of solution of magnesium in acid solutions. In experiments in which oxygen was not excluded, the progress of the reaction was followed by determining the loss in weight of different cylinders of metal after they had dissolved in solutions of the same initial composition for successively longer periods of time.

In Table XIII the results of such experiments with acetic and chloroacetic acids are compared with those obtained in the absence of oxygen. In the initial stages of the experiment the reaction rates were more rapid when oxygen was not excluded. But as the reaction proceeded it slowed down more rapidly due to the formation of water. The greater initial velocity was probably due to depolarization on the surface of the metal. This is the first time depolarization has been observed for magnesium.

TABLE XIII

EFFECT OF OXYGEN ON THE DISSOLUTION OF MAGNESIUM IN ACIDS AT 30°

Atmosphere, and gas in alcohol	10^5 equiv. per min. per sq. cm. Metal dissolved			
	Minutes 5	12	19	27
	0.12 *M* Acetic Acid			
Nitrogen	1.17	8.07	19.8	28.6
Air	4.25	12.8	17.0	23.0
	Minutes 5	12	18	25
	0.059 *M* Chloroacetic Acid			
Nitrogen	1.29	6.28	11.1	15.8
Air	1.48	8.69	10.1	15.0

Experiments were also carried out with mixtures of hydrochloric acid and lithium chloride, in which oxygen was not excluded. The results of these experiments are summarized in Table XIV. Most of the acid was consumed in accordance with the unimolecular reaction rate law. The unimolecular velocity constant is 0.242 cm. per min. The straight lines in Fig. 6, which were obtained by plotting log *a* − *x versus* time, illustrate how well the law was obeyed. In these experiments the amount of acid consumed always was found to be equivalent to the weight of metal which had been dissolved.

TABLE XIV

EXPERIMENTS AT 30° WITH MAGNESIUM AND HYDROCHLORIC ACID WITH OXYGEN NOT EXCLUDED

Concn. of acid, mole/l.	Concn. of lithium chloride, mole/l.	Slope of log $a-x$ *vs.* time	% Acid consd. via law
0.0275	0.0725	0.0430	78
.0388	.0612	.0473	76
.0408	.0000	.0427	59
.0626	.0374	.0511	88
.0636	.0864	.0421	55
.0679	.0000	.0430	82
.0926	.0000	.0524	82

Average slope = 0.0459.
k = 0.242 cm. per min.

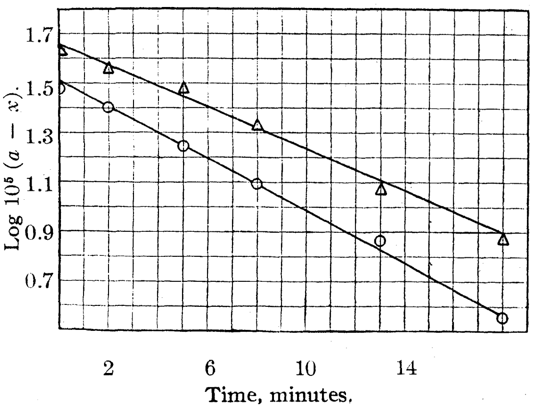

Fig. 6.—Relationship between log *a* − *x* and time for the solution of magnesium in hydrochloric acid when oxygen is not excluded. The circles and triangles show the points obtained with 0.0626 and 0.0679 *M* acid, respectively. The line for the latter solution is displaced upward 0.1 unit.

Short induction periods were expected here as in the experiments in which oxygen was excluded. That they were not detected was probably due to the method which had to be used to follow the progress of the reaction. After most of the acid had been consumed, the reaction velocity decreased too rapidly to obey the rate law, and no reaction with the solvent was detected. The apparent absence of this reaction is peculiar, when we consider that it occurred when magnesium dissolved in a solution of acetic acid containing lithium chloride in the presence of oxygen. However, the velocity constant is very similar to that for the solution of zinc in alcoholic hydrochloric acid, which is 0.217. And as we explained previously, this is exactly what we should expect if magnesium reacted only with the hydrochloric acid and if the observed reaction rate was governed by the rate at which the acid was transported to the surface of the metal.

We have already described how a very pure sample of zinc dissolved readily in alcoholic hydrochloric acid without the aid of a depolarizer. In contrast to this, it is commonly known that pure zinc scarcely dissolves in aqueous acids unless a depolarizer such as potassium nitrate is present.[23] From these results it appears that the discharge potential of hydrogen on zinc is smaller in alcohol than in water. For magnesium the reverse seems to be true, since we have already shown that oxygen hastens the solution of magnesium in alcoholic solutions, whereas depolarizers,[8,19] do not increase the velocities of solution of magnesium in aqueous acids.

In connection with these experiments, it might well be pointed out that one should be careful in the use of depolarizers, when measuring the rates of solution of metals in acids. Thus the data in Table XV show that lithium nitrate lowers the rates of solution of magnesium and zinc in aqueous acetic acid. In order to show this for zinc it was necessary to determine the effect of increasing the duration of different experiments with solutions of the same initial composition since the reaction scarcely proceeded in the absence of nitrate.

A more striking example of the effect may be observed in the behavior of zinc with alcoholic dichloroacetic acid solutions. Although zinc scarcely dissolved in solutions of acetic and chloroacetic acids, it did dissolve readily in 0.1 *M* dichloroacetic acid. No hydrogen was evolved, no titratable acid was consumed and considerable chloride ion was formed. This reaction, which seems to be similar to the Wurtz reaction, did not occur when the solution was 0.05 *M* in lithium nitrate. We consider these results evidence that nitrate ion can oxidize the surfaces of magnesium and zinc.

Data for similar experiments with aqueous mixtures of hydrochloric acid and lithium nitrate are also reported in Table XV. From this it is plainly seen that with hydrochloric acid a considerable side reaction occurs.

TABLE XV

EXPERIMENTS AT 30° WITH AQUEOUS MIXTURES OF ACIDS AND LITHIUM NITRATE

Concn. of acid, mole/liter	Concn. of nitrate, mole/liter	Length of expt., min.	Vel. const., *k*, cm./min.
Magnesium and Acetic Acid			
0.0353	0.00	20	0.368
.0785	.00	16	.369
.0785	.00	6	.315
Zinc and Acetic Acid			
0.0322	0.05	9	0.258
.0322	.05	27	.237
.103	.10	9	.236
.103	.10	27	.228
Magnesium and Hydrochloric Acid			
0.0298	0.00	12	1.058
.0500	.00	14	0.978
.0298	.05	3	.894
.0298	.05	7	.648
Zinc and Hydrochloric Acid			
0.0312	0.05	3	0.875
.0312	.05	6	.875
.0312	.05	9	.730
.0312	.05	12	.651
.0312	.10	3	.884
.0312	.10	12	.544
.103	.10	3	.592
.103	.10	12	.459

Although experiments of this type with alcoholic solutions are not reported in detail, because water was formed, we did find that lithium nitrate retarded the solution of magnesium in alcoholic hydrochloric and acetic acids.

Discussion

The following description of what occurs when a cylinder of magnesium is rotated in a solution of an acid in ethyl alcohol is based on the preceding experimental results.

The induction period probably starts with acid reacting and removing a coating from the surface of the metal. The acid is aided by chloride ion or chlorine compound if present. Chloroacetate ion (and like ions) aids also, when produced in the reaction. On those areas which have been cleaned the alcohol reacts. Ethylate ion is formed faster than acid approaches the surface of the metal. As a result the acid is neutralized before it reaches the metal, and the region adjacent to the metal is alkaline. The clean portions of the metal tend to become covered again with a coating of magnesium hydroxide, due to the water present, more rapidly than they can be cleaned by chloride ion, etc., as we have seen from the fact that the reaction rate decreases after the acid has been con-

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(23) This opportunity is taken to correct a statement by Kilpatrick and Rushton,[8] that potassium nitrate causes zinc to dissolve in aqueous acids more rapidly than magnesium. Our results agree more nearly, though not completely, with those of King and Braverman,[19] who found that the addition of nitrate raised the rates of solution of zinc to those of magnesium.

sumed. Since the region adjacent to the surface of the metal is alkaline, the acid cannot aid in this cleaning. Meanwhile, the rate of cleaning of surface with which alcohol is not reacting decreases, due to the decrease in the concentration of acid. When equal areas of the metal are being cleaned and covered in the same period of time, the clean area will have reached a maximum, and the maximum rate of reaction will be observed. The higher the initial concentration of an acid, the larger will be the quantity of acid consumed during the induction period and consequently the area of clean surface. This is what happens, as can be seen from the data in Tables III and VII. From the point of maximum reaction onward surface is covered more rapidly than cleaned.

The observed rate of reaction at any time depends on the area of clean surface. This, in turn, appears to be related to the concentration of ethylate ion adjacent to it. We should expect this to be so, since the concentration of ethylate ion next to the surface should be an important factor in determining the amount of magnesium hydroxide which forms on the metal due to the reaction with water. From the results of the experiments to determine the influence of temperature and the rate of stirring we should conclude as was pointed out previously, that the rate of disappearance of ethylate ion from the surface by transport of acid and ethylate ion only partially determines the concentration of ethylate at the reaction interface. It also depends on the actual rate of the chemical reaction between the magnesium and the alcohol molecules. That is, the two rates do not differ sufficiently in magnitude for one to be the sole rate-determining factor.

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Summary

1. It was found that magnesium can displace hydrogen from the molecules of ethyl alcohol without the intermediate formation of solvated proton.

2. When magnesium dissolves in solutions of acids in ethyl alcohol the predominant reaction is between the metal and the alcohol. The production of ethylate ion is sufficiently rapid to prevent other acids from reaching the metal.

3. The observed rate of reaction depends directly on what portion of the measured surface of the metal is available for reaction. This is related to the concentration of ethylate ion at the reaction interface, which is determined by two processes whose velocities do not differ sufficiently for either of them to be the sole rate-controlling factor. They are the actual rate of the chemical reaction between the metal and alcohol and the rate of removal of ethylate ion from the reaction interface by neutralization and transport.

PHILADELPHIA, PENNA. RECEIVED DECEMBER 29, 1936

NOTES

Ultramicroscopic Examination of Mixed Films

BY FREDERICK M. FOWKES, ROBERT J. MYERS AND WILLIAM D. HARKINS

The presence of a paraffin oil, such as nujol, in an expanded film formed by a fatty acid, such as myristic or pentadecylic acid, has a surprisingly great effect upon the pressure–area relations, as found by Myers and Harkins [R. J. Myers and W. D. Harkins, *J. Phys. Chem.*, **40,** 959 (1936); W. D. Harkins and R. J. Myers, THIS JOURNAL, **58,** 1817 (1936)]. This fact suggests that even if some of the paraffin oil is present in the form of lenses, a part remains mixed with the monomolecular film of acid. Myers and Harkins were unable to find any lenses visible to the naked eye in most of the mixed films investigated by them. In order to determine whether microscopic lenses are present, somewhat similar work has been done in which the pressure–area relations were determined by the Wilhelmy method and simultaneous observations of the structure of the film were made by the use of a dark field condenser and a microscope, as in the work of Zocher and Stiebel [*Z. physik. Chem.*, **147A,** 40 (1930)].

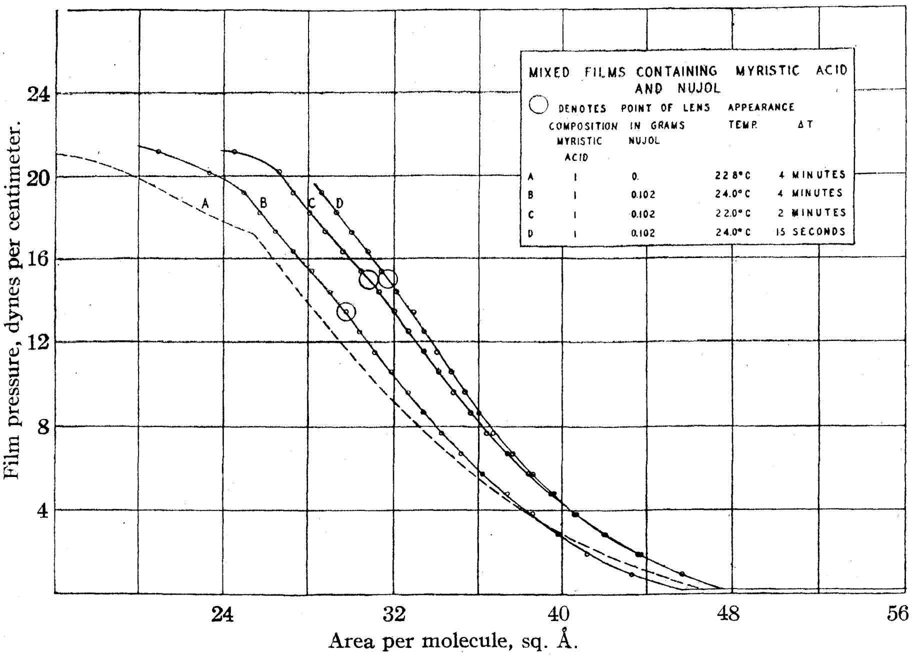

Fig. 1.

Mixtures of one part by weight of nujol to two parts of stearic, myristic, pentadecylic or oleic acids exhibit many oil lenses from gaseous film pressures up through collapse pressures. The average lens diameter in these films is about 1–2 μ and the lens concentration on an expanded film is of the order of 2000 lenses per sq. mm.

All films which contain a larger ratio of the paraffin oil to fatty acid give oil lenses, the lenses increasing in size as the relative concentration of the oil increases.

However, when mixtures which contain 0.3 or less parts of the paraffin oil to one part of fatty acid are examined, no lenses appear until the film is compressed to a certain critical pressure. At these points the lenses appear suddenly, their diameters seem to be less than 1 μ, and their concentration is of the order of 2500 lenses per sq. mm. If the pressure is decreased one or two dynes per cm. the lenses disappear, but reappear as before upon recompression. The force–area curves with nujol–myristic acid mixtures on 0.01 *m* hydrochloric acid show the dependence of the appearance of the lenses on film composition, film pressure and rate of compression. It probably depends also on the nature of the substrate.

The apparent compressibility of the film increases as the time of compression is increased (Fig. 1), but lenses first appear at areas which are largest for the most rapid compression. In both figures the line of dashes represents pure myristic

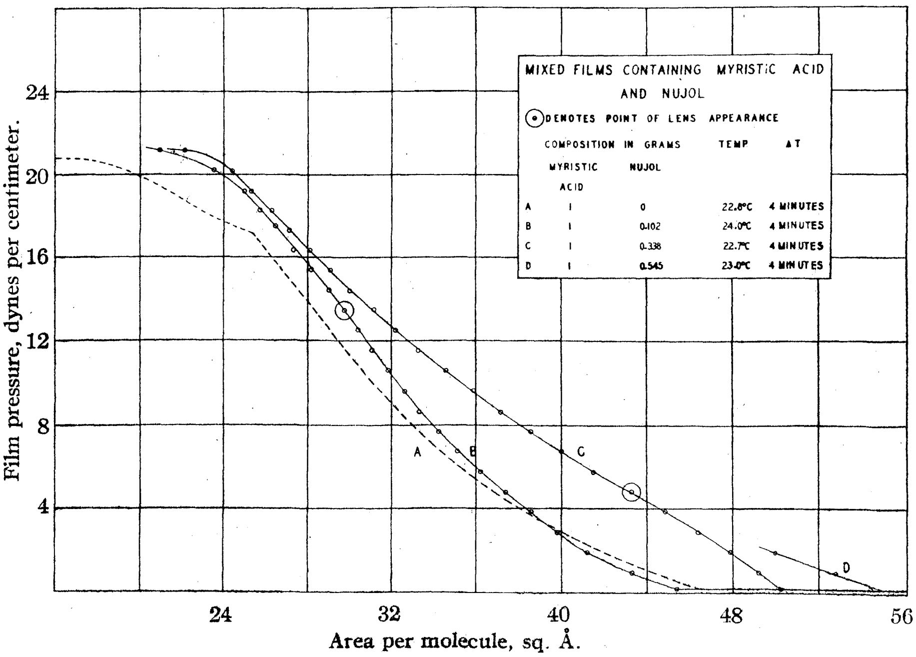

Fig. 2.

acid. All areas for the mixtures refer to the area per molecule of the acid, without reference to the amount of paraffin oil present.

From Fig. 2 it is obvious that at areas at which no lenses are visible, if the molecules of acid were to be oriented as in a condensed film, the total area would be more than sufficient to allow every molecule of the paraffin oil to be in contact with the water, but it is not suggested that the orientation is of this type. The presence of the oil causes these films to occupy larger areas, and Myers and Harkins have shown that larger amounts of oil expand the film at low pressures, but more greatly condense it at high pressures.

Thus it appears that uniform mixed films composed of fatty acids and liquid hydrocarbons may exist but these films are transformed at definite film pressures to composite films with lenses of hydrocarbon oil.

An investigation of these phenomena is in progress. An important feature revealed in this work is that the appearance of the lenses does not give rise to a discontinuity in the pressure–area curves.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

BAKER CHEMICAL LAB.
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RECEIVED FEBRUARY 23, 1937

Protein Content of the Bark of Black Locust, *Robinia Pseudacacia*

BY D. BREESE JONES AND SAMMIE PHILLIPS

The observations here recorded relate to the surprisingly large quantity of protein in the bark of the common black locust tree. Protein is a well-recognized constituent of most plants and animal tissues, but as far as known the black locust is the only tree from the bark of which protein has been isolated and studied.

In 1899, Power and Cambier[1] demonstrated that the protein of the black locust tree was responsible for the poisoning of horses which had gnawed the bark of this tree. Later, other investigators[2–4] found that hypodermic injections of a solution of this same crude protein preparation produced an alteration of the kidneys producing a nephritis, and that even in great dilutions it agglutinated the red corpuscles of the blood of many different animals. Several instances are recorded[5] where both people and animals have been poisoned by the bark of the locust tree.

In the work of the authors referred to only the crude protein coagulum was used. No attempt was made to study the chemical and physical properties of the bark proteins or to determine the amount of protein in the bark. In 1925, Jones and Gersdorff[5] found that the dried inner bark collected from two locust trees in Maryland contained 17.5% crude protein. This protein was found to consist chiefly of a globulin, albumin and a proteose. The physical properties and composition of the proteins isolated were similar to those of most vegetable and animal proteins. They contained practically the same assortment and proportions of amino acids as found in most proteins.

Occasion was recently had to examine the bark from a number of black locust trees grown in different localities. This bark was collected[6] in Ohio and Indiana from trees ranging in age from seven to ten years. The outer brown, suberous portion of the bark was carefully removed. Only the inner, light colored portion was employed. The latter was allowed to dry by exposure to the air, and then was ground to a coarse powder in a mill. Moisture in the ground bark was determined by heating for twenty-four hours at 110°. Nitrogen in the samples was determined by the Kjeldahl method, and the crude protein calculated by multiplying the percentage of nitrogen by the conventional factor 6.25. The percentages given in Table I are based on moisture-free material.

The quantity of protein found covers a rather wide range. The average, 21.5%, is, however, considerably higher than that previously found in this Laboratory when working with the bark from the trees grown in Maryland. This difference may be due to the fact that the barks were collected at different seasons of the year. The bark from the Maryland trees was collected about the middle of August, while that from the

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(1) F. B. Power and J. Cambier, *Pharm. Rundschau*, **8**, 29 (1890).

(2) C. Lau, "Uber vegetabilische Blut-Agglutinine," Inaugural dissertation, Rostock, 1901, p. 64.

(3) R. Kobert, *Landw. Vers.-Sta.*, **79–80**, 97 (1913).

(4) P. Ehrlich, *Klin. Jahrb.*, **6**, 315 (1898).

(5) D. B. Jones, C. E. F. Gersdorff and O. Moeller, *J. Biol. Chem.*, **64**, 655 (1925).

(6) The samples were collected under the supervision of Dr. Ralph C. Hall of the Bureau of Entomology and Plant Quarantine, to whom grateful acknowledgment is made. Some locust trees are seriously damaged by the locust borer. Other trees seem to be resistant to the attacks of this insect. Determinations of protein in the bark of resistant and susceptible trees were made with the idea that there might be a correlation between immunity to borer attack and the quantity of protein in the bark. No such correlation was found, however.

TABLE I

PROTEIN CONTENT OF THE BARK FROM 21 LOCUST TREES GROWN IN DIFFERENT SECTIONS

Series R

Samples of Series R were from borer-resistant trees.

Sample no.	Source	Time collected	Age of tree, yrs.	Protein content, %
R_1	Hopedale, Ohio	11-26-34	9	18.12
R_2	Hopedale, Ohio	11-26-34	9	25.34
R_3	Hopedale, Ohio	11-26-34	9	23.23
R_4	Hopedale, Ohio	11-26-34	9	20.38
R_5	Cambridge, Ohio	11-26-34	8	22.41
R_6	Cambridge, Ohio	11-26-34	8	20.93
R_7	Cambridge, Ohio	11-26-34	8	20.93
R_8	Cambridge, Ohio	11-26-34	7	20.81
R_9	Cambridge, Ohio	11-26-34	7	19.46
R_{10}	Cambridge, Ohio	11-26-34	7	22.68
R_{11}	Versailles, Ind.	11- 5-34	13	21.41
			Average	21.43

Series S

Samples of Series S were from borer-susceptible trees.

Sample no.	Source	Time collected	Age of tree, yrs.	Protein content, %
S_1	Minerva, Ohio	11-26-34	9	27.98
S_2	Minerva, Ohio	11-26-34	9	22.22
S_3	Minerva, Ohio	11-26-34	9	26.62
S_4	Minerva, Ohio	11-26-34	9	24.99
S_5	Minerva, Ohio	11-26-34	9	23.32
S_6	Hopedale, Ohio	11-26-34	10	12.94
S_7	Hopedale, Ohio	11-26-34	10	25.69
S_8	Hopedale, Ohio	11-26-34	10	15.87
S_9	Hopedale, Ohio	11-26-34	10	19.11
S_{10}	Hopedale, Ohio	11-26-34	10	17.06
			Average	21.58

Ohio and Indiana trees was collected the latter part of November. It has been shown[7] that soon before the leaves fall in the autumn their protein is transported to the parenchyma of the bark where it is stored during the dormant period.

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[7] E. Schulze, *J. Landw.*, **52**, 323 (1904).

PROTEIN AND NUTRITION RESEARCH DIVISION
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UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

RECEIVED JANUARY 11, 1937

The Existence of a Maximum in the Gas Solubility–Pressure Curve

BY I. R. KRICHEVSKY

Basset and Dodé[1] have measured the nitrogen solubility in water at 18° and under pressure up to 4500 kg./sq. cm. They detected an excessively interesting phenomenon, that at pressures about 3000 kg./sq. cm. the nitrogen solubility passes through a maximum. Though their determinations are not particularly exact, nevertheless the existence of a maximum is a reality and can be predicted theoretically.

For a case of slightly soluble gases in solvents with small vapor pressure we[2] have deduced a thermodynamical equation

$$\log f_2/N_2 = \log K + \overline{V}_2P/2303RT \qquad (1)$$

where f_2 is the fugacity of the gas, N_2 its mole fraction in the solution, K Henry's coefficient, $\overline{V}_2$ partial molal volume of the dissolved gas and P total pressure.

The solubility maximum corresponds to that pressure at which

$$\partial \ln N_2/\partial P = 0 \qquad (2)$$

Differentiating the equation (1) with respect to pressure and substituting V_2/RT for $\partial \ln f_2/\partial p$, where V_2 is gas volume, we can readily find that at the maximum solubility

$$V_2 = \overline{V}_2 \qquad (3)$$

The partial molal volume of the water-dissolved nitrogen at 18° is 32.7 cc.[2] For lack of data we shall accept that the partial molal volume of nitrogen does not depend upon pressure. Extrapolating data of Amagat[3] for nitrogen compressibility we found that at 18° the pressure of 3600 kg./sq. cm. corresponds to the volume of 32.7 cc., which is in a fairly good agreement with measurements of Basset and Dodé.

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[1] Basset and Dodé, *Compt. rend.*, **203**, 775 (1936).

[2] Krichevsky and Kasarnovsky, THIS JOURNAL, **57**, 2168 (1935).

[3] Amagat, *Ann. chim. phys.*, **29**, 68 (1893).

D. I. MENDELEYEFF CHEMICAL-TECHNOLOGICAL INSTITUTE
MOSCOW, U. S. S. R.

RECEIVED NOVEMBER 24, 1936

Mechanism of the Reduction of Unsaturated Compounds with Alkali Metals and Water

BY CHARLES BUSHNELL WOOSTER AND KENNETH L. GODFREY

A number of valuable methods for reducing unsaturated organic compounds involve the use of a combination of an alkali metal or its amalgam with water or some other hydrolytic solvent, and the various interpretations which have been offered for these reactions are based on one, or the other, of two rival hypotheses. The earlier of these hypotheses attributes the reduction to "nascent" hydrogen liberated by the reaction between the alkali metal (or its amalgam) and the hydrolytic solvent.[1] In more general terms, this hypothesis requires that the actual reduction is effected by the *combination* and not by the metal alone. The more recent hypothesis attributes the

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[1] Kekulé, *Ann. Suppl.*, **1**, 129 (1861); Herrmann, *Ann.*, **132**, 75 (1864); von Baeyer, *ibid.*, **269**, 145, 170, 174 (1892).

actual reduction to the alkali metal alone; that is, the primary reduction process is assumed to be addition of the alkali metal to the unsaturated compound. It is considered that the function of the solvent is merely to replace the metal in the addition compound with hydrogen by a hydrolytic process and that direct reaction between the solvent and the free alkali metal (or its amalgam) is a side reaction.[2] It has been shown definitely that certain specific reduction processes actually follow the course prescribed by the second hypothesis.[3]

We have now discovered another specific reduction reaction which appears definitely to follow the course prescribed by the *first* hypothesis. This reaction is the reduction of toluene with sodium (or potassium) and water in liquid ammonia. Toluene is not attacked by solutions of these alkali metals in liquid ammonia in the absence of water for the blue color of the alkali metal solutions is not discharged by addition of a large excess of toluene even when the mixture is allowed to stand for several hours. Furthermore, the presence of the total amount of metal in the free state may be demonstrated by the addition of ethyl bromide, ammonium chloride or a catalyst (iron rust) which initiates reaction between the metal and the solvent ammonia. Under these conditions the theoretical amount of ethane or hydrogen is always evolved and the toluene may be recovered. On the other hand, when water is added to the mixture much less than the theoretical amount of hydrogen is evolved and there is obtained a highly unsaturated liquid product which boils over the range 110–115°, chars with fuming sulfuric acid, reacts vigorously with liquid bromine and rapidly decolorizes a solution of bromine in carbon disulfide.

It is evident that although toluene does not react with liquid ammonia solutions of these alkali metals, it is immediately attacked (doubtless reduced) when water also is added. These facts are especially significant because under such conditions a very appreciable concentration of toluene is always present in the same phase with the ammonia and the alkali metal so the action of water cannot be ascribed to any purely surface phenomenon. It is also noteworthy that the effective combination is relatively specific, thus the hydrogen produced by reactions between the alkali metals and ammonia or ammonium chloride does not attack the toluene.

Finally, these observations have an important bearing on the technique of studying reactions in liquid ammonia, because two common practices are the use of toluene as a diluent to facilitate the reaction of organic substances sparingly soluble in ammonia, and the measurement of the hydrogen evolved on addition of water to determine the amount of excess free alkali metal remaining at the end of a reaction. It is now clear that a combination of these two practices will give misleading results, and that ammonium chloride (or an ammonolysis catalyst) should be used instead of water under such circumstances.

These studies are being continued in the hope of obtaining further significant information regarding the mechanism of such reduction processes.

CHEMICAL LABORATORY
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RECEIVED JANUARY 27, 1937

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[2] Willstätter, Seitz and Bumm, *Ber.*, **61**, 871 (1928).

[3] Wooster and Smith, THIS JOURNAL, **53**, 179 (1931).

COMMUNICATIONS TO THE EDITOR

OCCURRENCE OF ACETOVANILLONE IN WASTE SULFITE LIQUOR FROM CONIFEROUS WOODS

Sir:

Investigation of the products of alkaline degradation of waste sulfite liquor from the pulping of coniferous woods (mixture of spruce and balsam) on a large laboratory scale has disclosed the presence therein of acetovanillone (3-methoxy-4-hydroxyacetophenone) identical in every way with the synthetic product made from guaiacol acetate. *Anal.* OCH_3, 18.65; calcd. 18.68; m. p. 114.5°. Synthetic acetovanillone: m. p. 115°; mixed m. p. 114–115°. Semicarbazone: m. p. 165.5–166°; mixed m. p. 164.5–165.5°.

DIVISION OF INDUSTRIAL AND
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McGILL UNIVERSITY
MONTREAL, CANADA

IRENE K. BUCKLAND
GEORGE H. TOMLINSON, JR.
HAROLD HIBBERT

RECEIVED FEBRUARY 25, 1937

OCCURRENCE OF ACETONE AND SYRINGIC ALDEHYDE AS DEGRADATION PRODUCTS OF LIGNIN SUBSTANCES

Sir:

We wish to report two degradation products obtained from lignin substances. The first, acetone, has been obtained by a stepwise oxidation as well as by ozonization of formic acid spruce lignin and identified as acetone superoxide, dibenzalacetone, and acetone 2,4-dinitrophenylhydrazone, melting points 132.5°, 112°, and 128°, respectively. No lowering of melting point was found after admixture with authentic synthetic samples. The second product, syringic aldehyde, was isolated by the alkaline scission of sulfite liquor obtained from yellow birch wood and identified as follows. *Anal.* (1) Calcd. for $C_9H_{10}O_4$: C, 59.3; H, 5.5; OCH_3, 34.1; mol. wt., 183. Found: C, 59.1; H, 5.6; OCH_3, 33.8; mol. wt. (Rast method), 175.6. (2) M. p. 111.5–112° (corr.). (3) Semicarbazone, m. p. 185–186° (corr.). (4) Deep green coloration with ferric chloride. (5) Crystalline derivative with dimedone. All these properties are in entire agreement with those recorded by McCord, THIS JOURNAL, **53**, 4181 (1931).

DIVISION OF INDUSTRIAL AND
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McGILL UNIVERSITY
MONTREAL, CANADA

ALAN BELL
W. LINCOLN HAWKINS
GEORGE F. WRIGHT
HAROLD HIBBERT

RECEIVED FEBRUARY 25, 1937

NEW BOOKS

An Introduction to the Preparation and Identification of Organic Compounds. By ROBERT D. COGHILL, Assistant Professor of Chemistry, and JULIAN M. STURTEVANT, Instructor in Chemistry, Yale University. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York, N. Y., 1936. xiii + 226 pp. 14 × 21 cm. Price, $1.75.

The use of typical preparations as a means of introducing students to the theory and practice of laboratory technique in elementary organic chemistry has been recognized as the most feasible approach for the past hundred years. The corresponding employment of systematic methods of organic qualitative analysis as a means of instruction is much more recent, and may perhaps be said to have been initiated about 1900 through the efforts of the late Professor Samuel P. Mulliken at the Massachusetts Institute of Technology. Since the publication of his monumental work, appreciation of the value of this aspect of the subject as a means of instruction has been growing, as evidenced by the appearance of elementary books such as those of Clarke, Kamm, Shriner and Fuson, and others. No institution of learning can claim a first rank course in elementary organic chemical laboratory unless adequate attention is given to the identification as well as to the preparation of simple organic compounds.

Despite the present recognition of the equal importance of the study of both the synthetic and analytical aspects of organic laboratory instruction, there has been a surprising delay in the appearance of a laboratory manual placing both on an equal footing in the same volume. The present book is intended to fill this recognized need.

Apart from the necessary indices, appendices, etc., the 207 actual text pages of the volume are divided among three types of treatment: manipulative operations (both from synthetic and analytical viewpoint), 48 pages; synthetic preparations, 67 pages; and identification of organic compounds, 92 pages.

The synthetic section includes 42 experiments about equally divided between solids and liquids. In addition to many standard preparations included in all laboratory manuals several new selections are offered, including benzene from sodium benzoate, mandelic acid from benzaldehyde, *m*-chloronitrobenzene from *m*-nitroaniline, anthranilic acid from phthalimide, ethyl resorcinol from resorcinol *via* resacetophenone and subsequent Clemmensen reduction, *p*-nitrobenzoyl chloride from the acid and thionyl chloride, *p*-bromophenacyl bromide from bromobenzene *via p*-bromoacetophenone, and indigo from benzaldehyde *via o*-nitrobenzaldehyde. Each procedure is preceded by a short discussion and followed by questions. Both the manipulative and preparative sections are well written and fully illustrated with diagrams.

The analytical section is based upon a selected list of between three and four hundred of the most common and easily available organic compounds arranged to be identified by a set of tests according to a given key. After a short introductory chapter, the subject is discussed in three chapters entitled, respectively, analytical methods, 21 pages; classified list of compounds, 14 pages; and preparation of derivatives, 49 pages. In the list of compounds it is very unfortunate that the order and group headings reiterating the distinctive characteristics of each part were not carried along in the text, as the present arrangement requires an inconvenient amount of cross references to preceding pages for interpretation of the key. Selections of group tests are generally good, but the experienced analyst will miss some of the most useful methods, such as the use of the Duclaux number in the characterization of volatile fatty acids, the characterization of phenols by formation of aryloxyacetic acids, etc. The long chapter on derivatives is apparently intended to acquaint the student with a very large number of possible procedures rather than with their several advantages or disadvantages in the rigorous identification of a particular individual compound. Despite the breadth of treatment of this aspect, the text contains only three specific references to the periodical literature: the authors could well have afforded to be a little more helpful in extending the horizon of the better students.

A little knowledge is a dangerous thing. The difficulties of selection for a short treatment of the methods of identification of organic compounds are so severe that the educational world must be not too critical. The authors deserve congratulation on this somewhat daring experiment. It is sincerely to be hoped that the accessibility of this manual will result in immediate attention to the subject in all courses of organic instruction where the analytical aspect is not yet included.

Ernest H. Huntress

Cours de Chimie Industrielle. Tome III. **Metallurgie.** (Industrial Chemistry. Vol. III. Metallurgy.) By G. Dupont, Professor in the Faculty of Sciences of the University of Paris. Gauthier-Villars, Éditeur, 55 Quai des Grands-Augustins, Paris, France, 1936. iii + 357 pp. Illustrated. 16 × 25 cm. Price, 65 francs.

This third volume of Dupont's "Cours de Chimie Industrielle" is a brief (355 pages) and elementary French textbook of metallurgy, including smelting and refining, the laboratory technique of preparation and testing of metals and alloys, and some discussion of the uses of metals and a little statistical information. The elementary character of the discussion is illustrated by the fact that the whole subject of special alloy steels requires only one page with a mention of only nickel, chromium, copper and tungsten as elements which may be added to steel with advantage. In another part of the book the metallurgy of vanadium is disposed of in one-half page which includes the statement "The ferrovanadium is used, in small proportions, for the refining of iron and steel, which results in an appreciable improvement in the mechanical qualities." The cobalt steels are not merely ignored but their industrial significance is denied: "Cobalt has no applications as the metal; its properties are not, from this point of view, very different from those of nickel, and it is much more rare than the latter. On the other hand, cobalt has in its combinations two industrial uses: (1) the manufacture of smalt, silicate of cobalt, a very beautiful blue glass, used as a pigment; (2) the manufacture of various salts of cobalt, used especially as an oxidation catalyst in the drying of oils." The entire invention and development of the cryolite method of making aluminum is ascribed to Héroult, without even a mention of the name of Charles M. Hall.

It seems clear that an experienced metallurgist will have no need to consult this book and that an American student or beginner can find better books in English unless he is primarily interested in improving his knowledge of the French language.

Grinnell Jones

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. Meyer. Eighth Edition. System-Number 23, **Ammonium,** Parts 1–2. Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany, 1936. 602 pp. 17 × 25 cm. Price, RM. 28.00 + 42.25.

The ammonium radical is the only non-elementary ingredient of matter which has been allotted a separate "System-Number" in Gmelin's Handbook. This fact and the 602 pages devoted to this subject reflect the importance of ammonium in inorganic chemistry.

The major part of this volume, as would be expected, is occupied with the physical properties of ammonium salts and their solutions, and is replete with tables and diagrams, so that a wealth of information is presented in small compass and in easily accessible form. The literature has been covered for the first half of the volume to the end of February, and for the second half to the beginning of July, 1936.

It is indeed a great advantage to students of inorganic chemistry to have this mass of information on an important subject so completely and conveniently presented.

Arthur B. Lamb

Synthetic Inorganic Chemistry. A Course of Laboratory and Classroom Study for First Year College Students. By Arthur A. Blanchard, Ph.D., Professor of Inorganic Chemistry, Joseph W. Phelan, S.B., Late Professor of Inorganic Chemistry, and Arthur R. Davis, Ph.D., Assistant Professor of Chemistry, at the Massachusetts Institute of Technology. Fifth edition. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1936. xii + 379 pp. 25 figs. 15 × 24 cm. Price, $3.00.

The fact that this book is now in its fifth edition would indicate that it fulfills the purpose stated in its preface, namely, "to meet satisfactorily the problem of first-year college students in chemistry." The present edition differs from the previous ones in that "a very considerable portion of the text has been wholly rewritten and the entire text has been subjected to a revision and rearrangement. Specific new exercises and discussions which have been introduced include such topics as the determinations of vapor density and molecular weight, the standardization of acids and the titration of acids and bases, Faraday's law and the use of the p_H scale of hydrogen-ion concentration. Several new preparations have been introduced and a few of the old ones have been discontinued."

Chapter I includes a number of quantitative experiments such as the determination of the "Weight of a Liter of Oxygen" and the "Volume of Hydrogen Displaced by Zinc." One chapter is devoted entirely to the theory of ionization. The remaining chapters are divided into two parts: the first includes directions for preparing typical compounds of the different groups of elements, while the second describes various experiments to be carried out with these compounds. A rather extended appendix covers the preparation of reagents, a discussion of the electromotive series, and the periodic classification of the elements.

The authors state that "all students entering the Massachusetts Institute of Technology should have met an entrance requirement in chemistry. It is very discouraging to such students to be set at once to reviewing what they have already had, however much they may need the review. The nature, and the considerable freedom in the choice, of laboratory work solves this situation in a very satisfactory manner. A review of preparatory school work is of course necessary, but by bringing this in incidentally the sting of it is removed."

Undoubtedly the student who successfully performs the experiments outlined in this text and is able to deduce correct conclusions from his findings will have gained a thorough knowledge of the fundamental principles of chemistry so far as may be expected of first-year college students.

WILLIAM MCPHERSON

BOOKS RECEIVED

January 15, 1937–February 15, 1937

ERNEST BALDWIN. "An Introduction to Comparative Biochemistry." The Macmillan Company, 60 Fifth Avenue, New York, N. Y. 112 pp. $1.50.

GEORGE BARGER. "Organic Chemistry for Medical Students." Second edition. Gurney and Jackson. 33 Paternoster Row, London E. C. 1, England. 251 pp. 10/6 net.

W. FRANKENBURGER. "Katalytische Umsetzungen in homogenen und enzymatischen Systemen." Akademische Verlagsgesellschaft m. b. H., Sternwartenstrasse 8, Leipzig C 1, Germany. 444 pp. RM. 34.80; bound, RM. 36.00.

R. FRICKE AND G. F. HÜTTIG. "Hydroxyde und Oxyhydrate." Band IX, "Handbuch der allgemeinen Chemie," edited by Paul Walden. Akademische Verlagsgesellschaft m. b. H., Sternwartenstrasse 8, Leipzig C 1, Germany. 641 pp. RM. 57; bound, RM. 60.

L. GATTERMANN. "Laboratory Methods of Organic Chemistry." Translated by W. McCartney from the 24th German edition edited by Heinrich Wieland. The Macmillan Company, 60 Fifth Avenue, New York, N. Y. 435 pp. $4.50.

R. W. GURNEY. "Ions in Solution." The Macmillan Company, 60 Fifth Avenue, New York, N. Y. 206 pp. $3.00.

C. C. HEDGES AND H. R. BRAYTON. "Laboratory Manual of Inorganic Chemistry and Elementary Qualitative Analysis." Revised edition. D. C. Heath and Company, 285 Columbus Ave., Boston, Mass. 271 pp. $1.48.

CARL OPPENHEIMER. "Die Fermente und ihre Wirkungen. Supplement, Lieferung 6." W. Junk Verlag, Scheveningsche Weg 74, Den Haag, Holland. 160 pp. Dutch fl. 10.

JOSEPH ROSIN. "Reagent Chemicals and Standards, with Methods of Assaying and Testing Them." D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y. 530 pp. $6.00.

HENRY C. SHERMAN. "Chemistry of Food and Nutrition." Fifth edition. The Macmillan Company, 60 Fifth Avenue, New York, N. Y. 640 pp. $3.00.

FILEMON TANCHOCO. "Physical Chemistry." Benipayo Press, Manila, Philippine Islands. 87 pp.

HENRY TAUBER. "Enzyme Chemistry." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 243 pp. $3.00.

HUGH S. TAYLOR AND H. AUSTIN TAYLOR. "Elementary Physical Chemistry." Second Edition. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y. 664 pp. $3.75.

WAYNE E. WHITE. "Specific Tests for Use in the 'Qual.' Course." Obtainable from the Author, 1611 New Hampshire St., Lawrence, Kansas. 14 pp. $0.25.

LUDWIG VANINO, Editor. "Handbuch der präparativen Chemie. Ein Hilfsbuch für das Arbeiten im chemischen Laboratorium. II Band. Organischer Teil." Verlag von Ferdinand Enke, Hasenbergsteige 3, Stuttgart W, Germany. 887 pp. RM. 45; bound, RM. 48.

L. ZECHMEISTER AND L. V. CHOLNOKY. "Die chromatographische Adsorptionsmethode. Grundlagen, Methodik, Anwendungen." Verlag von Julius Springer, Schottengasse 4, Wien I, Austria. 231 pp. RM. 14.40.

"British Chemicals and their Manufacturers." The Official Directory of the Association of British Chemical Manufacturers. Published by and available only from the Association, 166 Piccadilly, London W 1, England. 466 pp. Gratis to genuine purchasers of chemicals.

"Statistical Appendix to Minerals Yearbook, 1935." U. S. Bureau of Mines. Superintendent of Documents, Government Printing Office, Washington, D. C. 486 pp. $1.25.

JOURNAL OF THE
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

2,3,6-Trimethylglucose Diethyl Mercaptal and its Use in the Preparation of 2,3,6-Trimethylglucose

BY M. L. WOLFROM AND LOUIS W. GEORGES[1]

2,3,6-Trimethylglucose has been synthesized from *d*-glucose by Irvine and Rutherford,[2] but the procedure employed is rather laborious for preparative purposes. The trimethylglucose can also be obtained as a hydrolytic product of methylated cellulose, methylated starch and a number of methylated disaccharides. The free sugar is very sensitive and is difficult to isolate in good yield. We have found that it forms a well-crystallized and easily isolable diethyl mercaptal, from which the free sugar can be regenerated under mild conditions and can thus be prepared readily in good purity.

In the work herein reported, methylated cellulose has been used as a source of 2,3,6-trimethylglucose. Irvine and Hirst[3] prepared this trimethylglucose by the treatment of methylated cellulose under pressure with methanol containing hydrogen chloride, and subsequent hydrolysis of the glycosidic methyl group. Denham and Woodhouse,[4] who first obtained crystalline 2,3,6-trimethylglucose, prepared it from methylated cellulose by direct hydrolysis with fuming hydrochloric acid. Hess and Neumann[5] likewise prepared this trimethylglucose by the hydrolysis of methylated cellulose with fuming hydrochloric acid, purifying the product through its methylglycoside.

In our experiments, methylated cellulose was hydrolyzed with fuming hydrochloric acid at low temperatures and the diethyl mercaptal of 2,3,6-trimethylglucose was isolated directly from the acid solution. This was an extension of the work previously reported from this Laboratory[6] on the hydrolysis of cellulose with fuming hydrochloric acid and mercaptalation at various stages of the hydrolysis. The free sugar was then regenerated from its diethyl mercaptal by treatment with mercuric chloride in moist acetone in the presence of cadmium carbonate.[7]

2,3,6-Trimethylglucose diethyl mercaptal is a readily crystallizable substance and forms a crystalline dibenzoate. There are thus added two crystalline derivatives to the rather small number recorded for this sugar. The diethyl mercaptal offers promise as a characterizing derivative for 2,3,6-trimethylglucose. The diethyl mercaptal of tetramethylglucopyranose was also obtained. This was an oil which formed a crystalline monobenzoate.

Experimental

Preparation of Methylated Cellulose.[8]—Commercial acetone-soluble cellulose acetate (20 g.; CH_3CO, 40%)[9]

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[1] Du Pont Cellulose Research Fellow.

[2] J. C. Irvine and Jean K. Rutherford, THIS JOURNAL, **54**, 1491 (1932).

[3] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123**, 518 (1923).

[4] W. S. Denham and Hilda Woodhouse, *ibid.*, **105**, 2357 (1914).

[5] K. Hess and F. Neumann, *Ber.*, **68**, 1360 (1935).

[6] M. L. Wolfrom and L. W. Georges, THIS JOURNAL, **59**, 282 (1937).

[7] M. L. Wolfrom, *ibid.*, **51**, 2188 (1929).

[8] We wish to acknowledge the assistance rendered by Messrs. M. E. Bernstein and R. D. Koons in the preparation of the methylated cellulose used in this work.

[9] Furnished through the courtesy of the du Pont Rayon Co., Waynesboro, Va. The viscosity of this material in 7% solution in acetone was 16.8 on the basis of an assigned viscosity of 100 for pure glycerol.

was methylated in one step to an approximate trimethyl cellulose according to the procedure employed by Haworth, Hirst and Thomas.[10] This method gave an average yield of 15 g. of the crude methylated product with a methoxyl content varying from 42 to 44%. This material was used without further purification in the subsequent hydrolytic experiments.

2,3,6-Trimethyl-*d*-glucose Diethyl Mercaptal.—Methyl cellulose (13.5 g.; OCH_3, 42–44%) was placed in a glass-stoppered pressure bottle and 200 cc. of fuming hydrochloric acid (d_4^{15} 1.202) added. Complete solution was effected by cooling to 0° and shaking. The solution, colored a pale amber, was allowed to stand at 4° for thirteen days. The solution had then acquired a dark-brown color which was removed by two treatments with Carboraffin, filtering each time through a layer of asbestos, previously treated with fuming hydrochloric acid. The final volume of the solution was adjusted with water to approximately 220 cc. and the solution divided into two 110-cc. portions for mercaptalation. Each portion was shaken mechanically for fifteen minutes at 0° with 14 cc. of purified ethyl mercaptan and was neutralized by pouring into a suspension of 107 g. of sodium bicarbonate in 170 cc. of water. During the neutralization a curdy precipitate formed. The mixture was kept overnight at ice-box temperature, filtered and dried in a vacuum desiccator over sodium hydroxide. The crude products from the two mercaptalations were combined and extracted with anhydrous ether. The ethereal extract was decolorized with Carboraffin, dried and the solvent removed; yield 10.5 g. of crystalline material. Pure material was obtained on recrystallization from petroleum ether (b. p. 65–110°); m. p. 71–72°; $[\alpha]^{29}$ $-15°$ (*c*, 3.8; $CHCl_3$).[11] The compound crystallizes in fine needles and is soluble in water, alcohol and the usual organic solvents.

Anal. Calcd. for $C_6H_9O_2(OCH_3)_3(SC_2H_5)_2$: S, 19.5; OCH_3, 28.3. Found: S (Carius), 19.3; OCH_3 (Kirpal and Bühn[12] method), 27.8.

Preparation of 2,3,6-Trimethyl-*d*-glucose from 2,3,6-Trimethyl-*d*-glucose Diethyl Mercaptal.—2,3,6-Trimethylglucose diethyl mercaptal (5.0 g.) was dissolved in acetone (30 cc.) containing water (0.8 cc.) and finely ground cadmium carbonate (4 g.) was added. A solution of mercuric chloride (16.0 g.) in acetone (30 cc.) was added gradually with mechanical stirring. The reaction was allowed to run at room temperature for twenty-four hours with occasional additions of fresh cadmium carbonate and acetone. The reaction mixture was then heated with stirring on a water-bath (40°) for fifteen minutes, filtered and the residue washed with acetone. The filtrate was concentrated in the presence of cadmium carbonate under reduced pressure at 35° to a viscous residue. This residue was extracted several times with warm chloroform until only a powder remained. The chloroform solution was filtered and then concentrated under reduced pressure at 35° to a sirup. The latter was dissolved in warm water and hydrogen sulfide passed into the cooled solution. The mercuric sulfide was removed by filtration, the filtrate aerated and the acid neutralized with solid sodium bicarbonate. The aqueous solution was then concentrated under reduced pressure at 40° to about one-third of the original volume. At this point inorganic salts began to separate and were removed by the addition of acetone to the solution and filtration. The filtrate was concentrated to a crystalline mass and the latter taken up in chloroform and the chloroform solution evaporated in a vacuum desiccator. The last traces of solvent were removed by stirring dry ether into the mass and evaporating under reduced pressure; yield, 2.6 g. The crystals so obtained were contaminated with a small amount of sirup, which was removed by two extractions with warm anhydrous ether; yield 2.0 g.; m. p. 104–108°. After one recrystallization from ordinary ether the melting point was 116–117°. Digestion of this material with cold, ordinary ether raised the melting point to 118–119°. The compound shows a downward mutarotation in aqueous solution and gave a final value after three and one-half hours of $[\alpha]^{26}$ $+68°$ (*c*, 1.7). The initial value after extrapolation to zero time was found to be $[\alpha]^{26}$ $+102°$. These constants identify the substance as 2,3,6-trimethylglucose of good purity.[13]

2,3,6-Trimethyl-*d*-glucose Diethyl Mercaptal 4,5-Dibenzoate.—2,3,6-Trimethylglucose diethyl mercaptal (1.0 g.) was benzoylated with pyridine (2 cc.) and benzoyl chloride (1 cc.) by standing at room temperature for twenty-four hours. Chloroform was added and the solution washed successively with 10% hydrochloric acid, aqueous sodium bicarbonate and water. The dried chloroform solution was concentrated under reduced pressure to a crystalline mass. Ether was added and the last traces of solvent removed under reduced pressure; yield 1.3 g. of crystalline material. The substance was obtained pure on recrystallization from ethanol; m. p. 115–116°; $[\alpha]^{23}$ $+61°$ (*c*, 4; $CHCl_3$). The compound crystallizes in glittering, elongated prisms and is soluble in ether, chloroform, acetone and benzene; is moderately soluble in alcohol; and is practically insoluble in water and petroleum ether.

Anal. Calcd. for $C_6H_7O_2(OCH_3)_3(COC_6H_5)_2(SC_2H_5)_2$: S, 11.9; C_6H_5CO, 39.1. Found: S, 11.6; C_6H_5CO,[14] 38.8.

2,3,4,6 - Tetramethyl - *d* - glucose Diethyl Mercaptal 5 - Benzoate.—Tetramethylglucopyranose[15] (3.0 g.) was dissolved in 30 cc. of concentrated hydrochloric acid (d^{15}_4 1.185) and the solution cooled to 0°. Ethyl mercaptan (6 cc.) was added and the mixture shaken at 0° for fifteen minutes, whereupon it was poured with stirring into a suspension of 30 g. of sodium bicarbonate in 75 cc. of water. The oily layer that separated was dissolved in chloroform and the mother liquor was extracted with chloroform. The combined extracts were dried, decolorized with Carboraffin and concentrated under reduced pressure to a thin sirup. Anhydrous ether was added and the solvent again removed under reduced pressure; yield 2.5 g. The sirup did not crystallize on standing for several weeks.

An amount of 2.5 g. of the sirupy tetramethylglucose diethyl mercaptal was benzoylated with pyridine (3 cc.) and benzoyl chloride (1.5 cc.) as described for the synthesis of

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[10] W. N. Haworth, E. L. Hirst and H. A. Thomas, *J. Chem. Soc.*, 821 (1931).

[11] All rotations are herein recorded to the D-line of sodium light.

[12] A. Kirpal and T. Bühn, *Ber.*, **47**, 1084 (1914).

[13] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121**, 1213 (1922).

[14] P. Brigl and H. Muehlschlegel, *Ber.*, **63**, 1551 (1930).

[15] Acknowledgment is made to Mr. D. R. Husted for the tetramethylglucopyranose preparation.

2,3,6-trimethylglucose diethyl mercaptal 4,5-dibenzoate and the product was crystallized in the same manner; yield 2.2 g. Pure material was obtained on crystallization from methanol by the addition of water; m. p. 64–65°; $[\alpha]^{21}$ +33° (*c*, 3.7; $CHCl_3$).

Anal. Calcd. for $C_6H_7O(OCH_3)_4(COC_6H_5)(SC_2H_5)_2$: S, 14.4; C_6H_5CO, 23.5. Found: S (Carius), 14.2; C_6H_5CO,[14] 23.2.

We wish to acknowledge our indebtedness to the E. I. du Pont de Nemours and Co., Inc., for the fellowship grant which has made this research possible.

Summary

1. 2,3,6-Trimethyl-*d*-glucose diethyl mercaptal, its dibenzoate and the monobenzoate of 2,3,4,6-tetramethyl-*d*-glucose diethyl mercaptal have been synthesized in crystalline condition.

2. 2,3,6-Trimethyl-*d*-glucose may be prepared readily by the hydrolysis of methylated cellulose with fuming hydrochloric acid, isolation of the sugar as its diethyl mercaptal and subsequent removal of the ethylmercapto groups.

COLUMBUS, OHIO RECEIVED JANUARY 18, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Cleavage of Diphenyl Ethers by Sodium in Liquid Ammonia. I. Ortho and Para Substituted Diphenyl Ethers

BY PAUL A. SARTORETTO AND FRANK J. SOWA

It has been found that a solution of sodium in liquid ammonia reacts vigorously and quantitatively with diphenyl ether. The reaction is complete when two atom equivalents of sodium is added to one mole equivalent of the ether. The products are mole equivalents of sodium phenate and benzene.

Conductivity experiments by Kraus[1] have shown that sodium is ionized in the medium of liquid ammonia, the metal being in equilibrium with sodium cations and electron anions. If reactivity involves sodium cations, a compound such as sodamide which is also ionized in liquid ammonia should cleave diphenyl ether; but it does not. Cleavage, therefore, involves either atomic sodium or the electron anions. Although there is no experimental proof favoring either, in a reduction of this type the electron anions are commonly thought of[2] as being the effective reagent. The mechanism of the reaction may be expressed as

$$\begin{gathered} ROR + 2Na^+ + 2e^- \longrightarrow Re^- + ROe^- + 2Na^+ \\ Re^- + NH_3 + Na^+ \longrightarrow RH + NH_2^- + Na^+ \end{gathered}$$

where (R) represents a phenyl group, and (e^-) an electron anion.

The purpose of this investigation was to use the above quantitative method to evaluate the effect of various substituents in the ortho and para positions. It was also employed to evaluate the effect of the ortho against the para position using the same substituent.

Experimental

For the preparation and physical properties of the substituted diphenyl ethers listed in Table I and used in this work the authors are indebted to John J. Verbanc for his assistance.

TABLE I

PHYSICAL PROPERTIES OF SOME DIPHENYL ETHERS

No.	Diphenyl ether	Yield, %	B. p., °C.	Mm.	M. p., °C.	Sp. gr., (25°C.)	$n^{25}D$
1	*p*-Nitro-	80	200	15	56–58		
2	*o*-Nitro-	70	185	8			
3	*p*-Amino-	99	188	14	83.5		
4	*o*-Amino-	99	170	18	44		
5	*o*-Methoxy-	60	288	745	76		
6	*p*-Methoxy-	55	125	5		1.1133	1.5762
7	*o,p'*-Dimethoxy-	55	203	20	77		
8	*o*-Methyl-	58	101	5		1.0468	1.5695
9	*p*-Methyl-	67	114	6		1.0450	1.5697
10	*o,p'*-Dimethyl-	54	121	7		1.0299	1.5640
11	*o*-Carboxy-	58			112–114		
12	*p*-Carboxy-	45			141		

(1) and (2) prepared according to the method of Brewster and Groening, "Organic Syntheses," John Wiley and Sons, New York, Vol. XIV, p. 67. (3) and (4) by the reduction of the corresponding nitro compounds employing the method of Suter, THIS JOURNAL, **51**, 2583 (1929). (5) and (6) prepared by heating 252 g. of guaiacol, 56 g. of potassium hydroxide and 2 g. of copper catalyst to 150° until all of potassium hydroxide dissolved. The water was distilled, any guaiacol that steam distilled was replaced. After adding 137 g. of bromobenzene the mixture was heated on an oil-bath for two and one-half hours at 220–230°. *p*-Methoxydiphenyl ether prepared by same procedure except phenol was used in place of guaiacol and *p*-bromoanisole in place of bromobenzene. (7) Similar to preparation (5) using guaiacol and *p*-bromoanisole and heated on an oil-bath for three hours. (8),

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[1] Kraus, THIS JOURNAL, **30**, 1323 (1908).

[2] Franklin, "The Nitrogen System of Compounds," Am. Chem. Soc. Monograph, 1935, p. 50.

(9) and (10) the procedure was the same as described under method (5) using the reagents phenol and *o*-bromotoluene for (8), phenol and *p*-bromotoluene for (9) and *o*-cresol and *p*-bromotoluene for (10). (11) Described by Brewster and Strain, THIS JOURNAL, **56**, 117 (1934). (12) *p*-Carboxydiphenyl ether was prepared from the *p*-methyldiphenyl ether by oxidation. Twenty-five grams of *p*-methyldiphenyl ether was stirred with 1300 cc. of water and 60 g. of potassium permanganate was added in 20-g. portions. The mixture was refluxed and stirred for eight hours. After treatment with dilute potassium hydroxide solution and extraction with ether, the mixture was acidified by adding sulfur dioxide. The *p*-carboxydiphenyl ether separated as white fluffy crystals. The compounds *p*-methoxydiphenyl ether, *o,p'*-dimethyldiphenyl ether were new compounds. The carbon and hydrogen analyses checked well with the calculated values.

A standard method of cleavage, described below, was followed throughout this work.

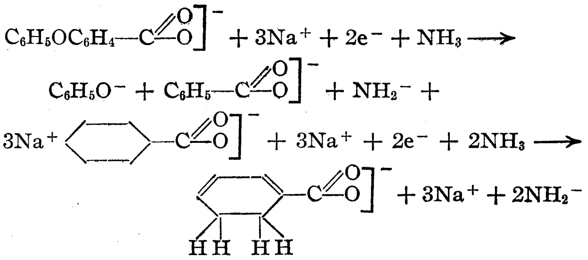
Cleavage of Diphenyl Ethers.—A 2-liter 3-necked flask was fitted with a mercury-sealed mechanical stirrer, liquid ammonia reflux condenser and a large spout dropping funnel. About 200 cc. of liquid ammonia was added to the flask and a solution of 0.25 mole of the diphenyl ether in 25 cc. of dry ethyl ether was introduced slowly. About 200 cc. of dry liquid ammonia was added to the dropping funnel, and to this was added 0.25 gram atomic weight of sodium. After a sufficient time was allowed for the sodium to dissolve, the solution was introduced into the reaction flask with constant stirring. Another 0.25 gram atomic weight of sodium was made to react in a similar manner. Completion of the reaction was indicated by the appearance of a permanent blue sodium–liquid ammonia coloration. The mixture was evaporated to dryness with the aid of a cold water-bath, hydrolyzed with water and acidified with dilute hydrochloric acid, substituting an ice-bath for the last two processes. The cleavage products were extracted with ether and analyzed, each according to a method thought most suitable.

In Table II the cleavage products and methods of analysis are listed for each cleavage. For brevity, the groups attached to oxygen of the ether are designated as (R) and (R'). In every case the yield was based upon the phenolic products, for it was found that products such as benzene and toluene were short of theoretical recovery, due to loss in entrainment with ammonia gas evolving from heat of reaction.

Discussion of Experimental Results

The cleavage of the above diphenyl ethers requires two atom equivalents of sodium with the exception of the carboxydiphenyl ethers.

4-Carboxydiphenyl ether reacts with approximately 5 atom equivalents of sodium, the last two atom equivalents reacting slowly. The mechanism for the reaction, based on the supposition that sodium reacts slowly with sodium benzoate in liquid ammonia,[3] and also that the sodium salt of the carboxydiphenyl ether reacts with 4 atom equivalents of sodium to form hydrogenated benzoic acid and phenol, is as follows



The second reaction is to be investigated further.

The cleavage of 2-carboxydiphenyl ether required approximately 4 atom equivalents of sodium, with incomplete hydrogenation of sodium benzoate.

In mono-substituted diphenyl ethers the linkage between the oxygen and the substituted phenyl group is strengthened against cleavage by sodium in liquid ammonia by the introduction of the following substituents, listed according to their increasing effectiveness: *o*-CH_3, *p*-CH_3, *p*-OCH_3, *o*-NH_2, *p*-NH_2; and the linkage is weakened toward cleavage by the following substituents, similarily listed: *o*-OCH_3, *o*-COONa, *p*-COONa. The results of cleavage of 2,4'-disubstituted diphenyl ethers, using the same substituent in each phenyl group, are in accord with those results expected from the knowledge of cleavage of mono-substituted diphenyl ethers.

In all the cleavages studied that are comparative, it has been indicated that a substituent, either hindering or facilitating cleavage of the linkage between oxygen and the substituted phenyl group, is more effective in para position than in ortho position.

Theoretical Discussion

Unequal amount of cleavage on each side of the oxygen to carbon linkage in substituted diphenyl ethers indicates that the electronic configuration of the carbon atoms directly linked to oxygen has been disturbed by the effects of the substituents. Since the electron (or sodium atom) may be considered as a nucleus seeking reagent, it will attach itself more readily to the carbon atom, linked to oxygen, which has the lowest electron density. In the mono-substituted diphenyl ethers, containing a substituent of the first series mentioned above, the electron attaches itself more readily to the phenyl group

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(3) Kraus and White, THIS JOURNAL, **45**, 768 (1923).

TABLE II

Compound ROR′		Method of analysis of cleavage products	Cleavage products as mole %	
R	R′		ROH	R′OH
Phenyl	Phenyl	Fractional distillation	100% Phenol	
Phenyl	4-Methylphenyl	Iodometric titration[a]	25.6 Phenol	74.9 *p*-Cresol
Phenyl	2-Methylphenyl	Iodometric titration	47.1 Phenol[b] 46 Phenol	52.9 *o*-Cresol 54 *o*-Cresol
2-Methylphenyl	4-Methylphenyl	Indices of refraction[c]	39 *o*-Cresol	61 *p*-Cresol
Phenyl	4-Methoxyphenyl	Fractional distillation	19 Phenol[d]	81 *p*-Methoxyphenol
Phenyl	2-Methoxyphenyl	Fractional distillation	55 Phenol[d]	45 Guaiacol
2-Methoxyphenyl	4-Methoxyphenyl	Fractional distillation	1 Guaiacol[d,e]	99 *p*-Methoxyphenol
Phenyl	4-Aminophenyl	Fractional crystallization	....	100 *p*-Aminophenol
Phenyl	2-Aminophenyl	Fractional crystallization	1 Phenol[f]	99 *o*-Aminophenol
Phenyl	4-Carboxyphenyl	Phys. prop. of phenol; m. p. acid; amide	100 Phenol[g]	....
Phenyl	2-Carboxyphenyl	Phys. prop. of phenol; m. ps. of acids	90 Phenol[h]	

[a] Redman and Weith, Brock, *J. Ind. Eng. Chem.*, **5**, 831 (1913). [b] Two cleavages were performed. [c] Plotting indices of refraction, at constant temperature, of known composition of ortho- and para- cresol mixtures, against percentage composition, a straight line was obtained, from which the composition of the unknown mixture was obtained. Suggested by Dr. A. J. Boyle. [d] Yield of anisole served as check. [e] Just a trace of guaiacol obtained. [f] Just a trace of phenol obtained. [g] Approximately theoretical amount of dihydrobenzoic acid obtained. [h] A mixture of dihydrobenzoic and benzoic acid obtained, which was short of the theoretical yield; *p*-hydroxybenzoic acid was not isolated, consequently the analysis was based on phenol.

that does not contain the substituent. It is reasonable to assume that the electronic configuration of the carbon atom, to which the electron attaches itself more readily, has not been disturbed appreciably by the substituent in the opposite phenyl group. Therefore, the electron density of the carbon atom (of the substituted phenyl group), which is attached to oxygen, has increased by the introduction of a substituent of the first series. On the other hand, the second series of substituents decrease the electron density of the carbon atom (of the substituted phenyl group) attached to oxygen.

Interpreting the experimental data in the light of electronic theories of Ingold,[4] Robinson,[5] etc., the influence of various substituents upon the carbon atoms in a phenyl group consists of two factors: an inductive effect, and a tautomeric effect. The effects observed in the case of the first series of substituents are in agreement with the application of these theories to such cleavage reactions and indicate that the tautomeric effect is the more dominating effect, and more pronounced in para than in ortho position; while the effect of the ortho substitution of OCH_3 group can be explained only by assuming that the inductive effect of the OCH_3 dominates the tautomeric effect, in this particular instance. This assumption is further substantiated by the cleavage of 2,4′-dimethoxydiphenyl ether. It is not in accord with the usual views, although it is to be expected that the inductive effect would be more pronounced in ortho than in para position.

The authors wish to express their appreciation to Dr. Andrew J. Boyle for his helpful suggestions.

Summary

Sodium in liquid ammonia cleaves diphenyl ethers rapidly and quantitatively at the carbon–oxygen linkage.

In mono-substituted diphenyl ethers, the tendency for the linkage between oxygen and the substituted phenyl group to cleave is decreased by the introduction of the following substituents, listed according to their increasing effectiveness: *o*-CH_3, *p*-CH_3, *p*-OCH_3, *o*-NH_2, *p*-NH_2. The tendency for the linkage between oxygen and the substituted phenyl group to cleave is increased by the introduction of the following substituents, similarly listed: *o*-OCH_3, *o*-COONa, *p*-COONa. The results of cleavage of 2,4′-disubstituted diphenyl ethers, using the same substituent in each phenyl group, are in accord with those results expected from the knowledge of cleavage of mono-substituted diphenyl ethers.

In all the cleavages studied that are compara-

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(4) (a) Ingold and Ingold, *J. Chem. Soc.*, 1310 (1926). (b) Ingold, *Chem. Rev.*, **15**, 225 (1934).

(5) Robinson and others, *J. Chem. Soc.*, 401 (1926).

tive, it has been indicated that a substituent, either hindering or facilitating cleavage of the linkage between oxygen and the substituted phenyl group, is more effective in para position than in ortho position.

NOTRE DAME, INDIANA RECEIVED DECEMBER 24, 1936

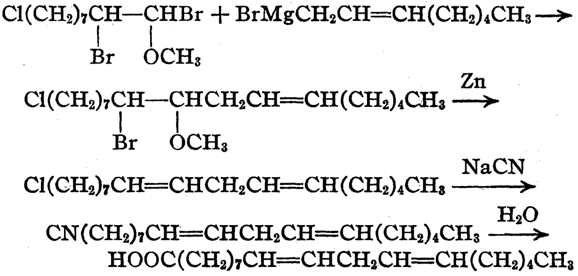
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Synthesis of Unsaturated Fatty Acids. II. Linoleic and 11-*n*-Amyl-9,12-tridecadienoic Acids

BY C. R. NOLLER AND M. D. GIRVIN

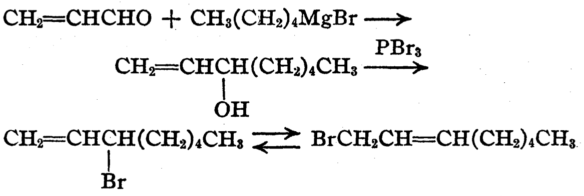
The synthesis of linoleic acid (9,12-octadecadienoic acid) is desirable not only because the commonly accepted structure is periodically questioned[1] but also because linoleic acid is apparently one of the accessory food factors, designated by Evans and his co-workers[2] as vitamin F, which is necessary for the growth and fertility of both male and female rats.

Using the following series of reactions which is similar to that previously used for the synthesis of oleic and elaidic acids[3] we have succeeded in synthesizing a product which contains α-linoleic acid.



$$\underset{\text{Br}}{\text{Cl(CH}_2\text{)}_7\text{CH}}\text{—}\underset{\text{OCH}_3}{\text{CHBr}} + \text{BrMgCH}_2\text{CH=CH(CH}_2\text{)}_4\text{CH}_3 \longrightarrow$$
$$\underset{\text{Br}}{\text{Cl(CH}_2\text{)}_7\text{CH}}\text{—}\underset{\text{OCH}_3}{\text{CH}}\text{CH}_2\text{CH=CH(CH}_2\text{)}_4\text{CH}_3 \xrightarrow{\text{Zn}}$$
$$\text{Cl(CH}_2\text{)}_7\text{CH=CHCH}_2\text{CH=CH(CH}_2\text{)}_4\text{CH}_3 \xrightarrow{\text{NaCN}}$$
$$\text{CN(CH}_2\text{)}_7\text{CH=CHCH}_2\text{CH=CH(CH}_2\text{)}_4\text{CH}_3 \xrightarrow{\text{H}_2\text{O}}$$
$$\text{HOOC(CH}_2\text{)}_7\text{CH=CHCH}_2\text{CH=CH(CH}_2\text{)}_4\text{CH}_3$$

The 1-bromooctadecene-2 from which the Grignard reagent was prepared was obtained by the series of reactions



$$\text{CH}_2\text{=CHCHO} + \text{CH}_3\text{(CH}_2\text{)}_4\text{MgBr} \longrightarrow$$
$$\text{CH}_2\text{=CH}\underset{\text{OH}}{\text{CH}}\text{(CH}_2\text{)}_4\text{CH}_3 \xrightarrow{\text{PBr}_3}$$
$$\text{CH}_2\text{=CH}\underset{\text{Br}}{\text{CH}}\text{(CH}_2\text{)}_4\text{CH}_3 \rightleftarrows \text{BrCH}_2\text{CH=CH(CH}_2\text{)}_4\text{CH}_3$$

It was realized at the outset that a mixture of 1-bromooctadecene-2 and 3-bromooctadecene-1 would result but the work of Winstein and Young[4] on analogous compounds indicated that the primary bromide would be formed in larger amount. Moreover, it was expected that the products arising from the secondary bromide would be the lower boiling and would be partially removed during the purification of the intermediate products of the synthesis.

The final product of the synthesis had the correct neutralization equivalent, iodine value, and molecular refraction for linoleic acid. Bromination of the product, however, gave none of the solid tetrabromide characteristic of α-linoleic acid. Since in the synthesis of oleic and elaidic acids[3] the equilibrium mixture of the two stereoisomers was obtained, it seemed unlikely that a mixture now had been obtained in which the geometrical isomer corresponding to α-linoleic acid was missing. Nevertheless a quantity of the synthetic material was elaidinized with Poutet's reagent[5] and the product again treated with bromine. Again no solid tetrabromide was obtained.

A portion of elaidinized product was next oxidized with permanganate according to the modified Hazura procedure used by Green and Hilditch[6] when a quantity of tetrahydroxystearic acids was obtained from which both α- and β-sativic acids were isolated. This proves definitely that α-linoleic acid was present. The amount of crude tetrahydroxy acids was about seven-tenths of that obtained from a sample of elaidinized natural α-linoleic acid and this would indicate that the amount of α-linoleic acid present in the synthetic mixture was of the order of 70%. The crude hydroxy acids from the synthetic product, however, were quite gummy and the total amount of once recrystallized product was only about 28% of that obtained from the natural product.

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(1) Takahashi, *J. Chem. Soc. Japan*, **42**, 130 (1921); *C. A.*, **15**, 2273 (1921); Haworth, *J. Chem. Soc.*, 1456 (1929); Nunn and Smedley-McLean, *Biochem. J.*, **29**, 2742 (1935).

(2) Burr and Burr, *J. Biol. Chem.*, **82**, 345 (1929); **86**, 587 (1930); Burr, Burr and Miller, *ibid.*, **97**, 1 (1932); Evans and Lepkovsky, *ibid.*, **96**, 143 (1932); Evans, Lepkovsky and Murphy, **106**, 431, 441, 445 (1934).

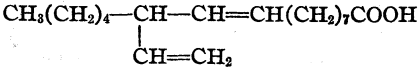
(3) Noller and Bannerot, THIS JOURNAL, **56**, 1563 (1934).

(4) Winstein and Young, *ibid.*, **58**, 104 (1936).

(5) Griffiths and Hilditch, *J. Chem. Soc.*, 2315 (1932).

(6) Green and Hilditch, *Biochem. J.*, **29**, 1554 (1935).

The other constituent of the synthetic mixture is undoubtedly 11-*n*-amyl-9,12-tridecadienoic acid



$$CH_3(CH_2)_4\text{—}\underset{\displaystyle CH{=}CH_2}{\underset{|}{CH}}\text{—}CH{=}CH(CH_2)_7COOH$$

arising from the 3-bromooctadecene-1. Ozonation gave an amount of formaldehyde corresponding to 16% of the calculated amount for this compound. Pure undecylenic acid, however, under the same conditions gave only 44% of the calculated amount of formaldehyde so that as high as 30% of the second isomer is indicated. It was noted that the synthetic product did not become viscous when exposed to air as readily as did α-linoleic acid and it is likely that a large amount of α-linoleic acid in the synthetic product was lost during the course of the numerous fractional distillations by which it was hoped to remove the lower boiling isomer.

The amount of synthetic material obtained during the course of this work was not sufficient for feeding experiments. Because of the numerous steps, poor yields and uncertainty concerning the exact composition of the product, it would seem desirable to develop a more satisfactory method of synthesis rather than attempt to produce synthetic linoleic acid in quantity by this method.

Experimental

***n*-Amylvinylcarbinol** was prepared from *n*-amylmagnesium bromide and acrolein in 47–49% yields observing the precautions recommended by Bouis.[7] After two fractionations the main product boiled at 78–81° at 20 mm. This alcohol has been prepared previously by Levene and Walti[8] who give the boiling point as 81–82° at 20 mm. but give no details concerning the preparation.

1-Bromooctadecene-2 and 3-Bromooctadecene-1.—A mixture of these bromides was prepared from the above alcohol and phosphorus tribromide according to the procedure of Bouis.[7] The yield of product, b. p. 87–89° at 20 mm., was 79%; $n^{23}\text{D}$ 1.4768; d^{23}_4 1.1314.

Anal. Calcd. for $C_8H_{15}Br$: Br, 41.88. Found: Br, 41.70, 41.85.

Because of the high boiling point and the ease with which rearrangement takes place,[4] no attempt was made to separate the mixture into pure isomers. On rapid redistillation at 20 mm. the first 5 cc. of distillate showed $n^{23}\text{D}$ 1.451 and the last 5 cc. $n^{23}\text{D}$ 1.477. After long standing the equilibrium value was $n^{23}\text{D}$ 1.472. Assuming the first and last fractions to be pure secondary and primary bromides, respectively, the equilibrium mixture would contain about 80% of the primary bromide.

1-Chloroheptadecadiene-8,11 and 1-Chloro-10-*n*-amyldodecadiene-8,11.—The mixed bromides were converted into the Grignard reagent in 75% yields, condensed with 8,9-dibromo-9-methoxynonyl chloride, and the bromine and methoxyl groups removed according to the procedure previously used for the synthesis of 1-chloroheptadecene-8.[3] None of the intermediate product was isolated in a pure state and the over-all yield based on the ω-chlorononylaldehyde was 12–15% boiling at 165–171° at 6 mm. after three fractional distillations; $n^{24}\text{D}$ 1.4604; d^{24}_4 0.8912; mol. ref. calcd., 84.6; found, 83.4.

Anal. Calcd. for $C_{17}H_{31}Cl$: Cl, 13.1; iodine no., 187.6. Found: Cl, 13.0; iodine no., 185.8.

A large amount of low boiling material was obtained which was not investigated.

1-Cyanoheptadecadiene-8,11 and 1-Cyano-10-*n*-amyldodecadiene-8,11.—To 12 g. of the mixed chlorodienes in 90 cc. of 95% alcohol was added 3 g. of sodium cyanide and the mixture refluxed for ninety-six hours. The sodium chloride was filtered from the solution and washed with alcohol, the alcohol distilled from the filtrates, and the residue fractionated under reduced pressure. There was obtained 7 g. (60.5%) b. p. 160–170° at 6 mm. Refractionation gave 5 g. (43%) of b. p. 165–170° at 6 mm.

Anal. Calcd. for $C_{18}H_{31}N$: N, 5.36; iodine no., 194.3. Found: N, 5.21; iodine no., 194.8.

9,12-Octadecadienoic and 11-*n*-Amyl-9,12-tridecadienoic Acids.—A solution of 7 g. of nitrile, 2 g. of sodium hydroxide in 10 cc. of water, and 90 cc. of 95% alcohol was refluxed for one hundred and twenty hours. The alcohol was distilled, the residue taken up in 200 cc. of water and extracted three times with petroleum ether. The aqueous solution was acidified and the acids extracted. The solvent was removed and the residue fractionated under reduced pressure. There was obtained 3 g. (40%); b. p. 200–205° at 6 mm. or 185–187° at 3 mm.; $n^{27}\text{D}$ 1.4640; d^{27}_4 0.8948; mol. ref. calcd. 85.9; found: 86.4.

Anal. Calcd. for $C_{17}H_{31}COOH$: neut. equiv., 280.2; iodine no., 180.8. Found: neut. equiv., 281.4; iodine no., 179.2.

The synthetic product after standing for several days at 10° deposited a small amount of solid which after filtration and recrystallization from petroleum ether melted at 59–61° and was saturated to bromine. It was thought that the prolonged heating with alkali may have converted some of the linoleic acid into palmitic or myristic acids, but mixed melting point determinations showed that the solid compound was not either. It was not investigated further.

Chemical Investigation of the Synthetic Product.—Bromination in petroleum ether under conditions that readily yielded the characteristic tetrabromide from natural α-linoleic acid[9] gave no solid bromide. The same results were obtained on samples of the synthetic and natural acids after isomerization with Poutet's reagent.[5]

Oxidation of 1.0 g. of isomerized natural α-linoleic acid by potassium permanganate according to the modified

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(7) Bouis, *Ann. chim.*, [10] **9**, 407 (1928).

(8) Levene and Walti, *J. Biol. Chem.*, **94**, 593 (1931).

(9) Natural α-linoleic acid used for comparison purposes was prepared from cottonseed oil through the tetrabromide (m. p. 114.5–115°) and the methyl ester by Rollett's procedure [*Z. physiol. Chem.*, **62**, 414 (1909)]. It was noted in another run where debromination of the tetrabromide was carried out in the absence of acid and without going through the methyl ester that the product solidified in the cold room at 10°. The highest melting point previously recorded for pure α-linoleic acid is −7° [Holde and Gentner, *Ber.*, **58**, 1067 (1925)] and we hope to investigate this product further.

Hazura procedure recommended by Hilditch[6] gave 0.57 g. of solid tetrahydroxystearic acids. Hilditch states that the tetrahydroxy acids were "separated by fractional crystallization from ethyl acetate." We used absolute ethyl acetate and found that the lower melting acid could be extracted and recrystallized from this solvent but that the higher melting acid was too insoluble to be recrystallized from it. After extraction of the lower melting acid with absolute ethyl acetate, the higher melting acid was recrystallized from 95% alcohol. There was obtained in this way 0.28 g. of tetrahydroxystearic acid, m. p. 156–157° and 0.07 g., m. p. 172–175°. When 1.0 g. of the synthetic acid was treated in exactly the same way there was obtained 0.40 g. of a sticky product from which was isolated only 0.08 g. of m. p. 151–154° and 0.02 g., m. p. 174–175°. Mixed melting points with the corresponding acids from natural α-linoleic acid were 152–155° and 173–175°.

A solution of 1.536 g. (0.00548 mole) of synthetic acids in 20 cc. of absolute ethyl acetate was ozonized and the solution decomposed with zinc dust and water according to the procedure of Whitmore and Church[10] without removal of the solvent. After distillation and extraction of the aqueous layer with ethyl acetate the formaldehyde was estimated iodimetrically.[11] A blank run was made in which 20 cc. of ethyl acetate was ozonized for the same length of time and decomposed in the same manner as the sample. The amount of formaldehyde from the sample, corrected by the blank, was 0.000883 mole, indicating the presence of 16% of 11-*n*-amyl-9,12-tridecadienoic acid. Pure undecylenic acid, however, gave only 44% of the calculated amount of formaldehyde under the same conditions. The water–zinc dust decomposition of the ozonides does not seem to be very satisfactory for compounds giving water insoluble products since the latter tend to coat the zinc dust and cause it to agglomerate.

The formaldehyde was identified positively by conversion into the 2,4-dinitrophenylhydrazone which after four crystallizations from methyl alcohol melted at 158–162°. The mixed melting point with pure formaldehyde-2,4-dinitrophenylhydrazone (m. p. 166–167°) was 159–163°.

An attempt to isolate the *n*-hexoic and *n*-heptoic acids which also should be formed on ozonation of the synthetic product gave a small amount of mixed acids distilling at 200–260° but conversion to the anilides gave an oil which could not be made to crystallize.

Summary

A series of reactions has been carried out which led to the synthesis of a mixture of linoleic acid and 11-*n*-amyl-9,12-tridecadienoic acid.

STANFORD UNIVERSITY, CALIF.

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[10] Whitmore and Church, THIS JOURNAL, **54**, 3712 (1932).

[11] Feinberg, *Am. Chem. J.*, **49**, 89 (1913).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Studies of Absorption Spectra. I. Crotonaldehyde and Acrolein

BY FRANCIS E. BLACET, WILLIAM G. YOUNG AND JACK G. ROOF

In connection with problems in photochemistry and in the synthesis of pure stereoisomeric compounds, a quantitative study of the absorption spectra of crotonaldehyde and acrolein in the vapor phase has been made. The object of this investigation was (1) to determine the types of absorption in different regions of the spectrum, (2) to compare the absorption of these two closely related compounds, and (3) in the case of crotonaldehyde, to test by spectroscopic means for the presence of *cis*-crotonaldehyde in the purified commercial product.

Although a number of investigators have studied these compounds,[1] the work for the most part was done with solutions in which the band structure of absorption, as shown by the vapors, was not observed. However, two exceptions to this generalization should be mentioned. Lüthy[1c] reported the fine structure but did not attempt to calculate extinction coefficients from studies of the vapor phase. Eastwood and Snow[1h] also have done nothing with extinction coefficients, but by means of a 21-foot (6.3 meter) grating have shown that some of the prominent maxima of acrolein may be resolved into very narrow bands which they attribute to rotational levels in the molecule.

Experimental Part

Purification and Treatment of Samples.—In an attempt to detect the presence of *cis*-crotonaldehyde in the purified commercial product, samples were prepared in two different ways and their absorption spectra studied. The first of these, which is hereafter called the "original" sample, was made in such a way that any mixture of the *cis* and *trans* forms would be preserved. The second or "irradiated" sample was treated with hydrochloric acid and sunlight by a procedure which is known to cause similar compounds to be converted into the *trans* form.[2]

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[1] (a) Bielecki and Henri, *Ber.*, **46**, 3627 (1913); (b) Purvis and McClelland, *J. Chem. Soc.*, **103**, 433 (1913); (c) Lüthy, *Z. physik. Chem.*, **107**, 284 (1923); (d) Henri, *Compt. rend.*, **178**, 844 (1924); (e) Purvis, *J. Chem. Soc.*, **127**, 9 (1925); (f) Henri, *Compt. rend.*, **199**, 849–851 (1934); (g) Thompson and Linnett, *Nature*, **134**, 937 (1934); (h) Eastwood and Snow, *Proc. Roy. Soc.* (London), **A149**, 446 (1935).

[2] (a) Wislicenus, *Ann.*, **248**, 341 (1889); (b) Blaise, *Ann. chim. phys.*, [8] **11**, 116 (1907).

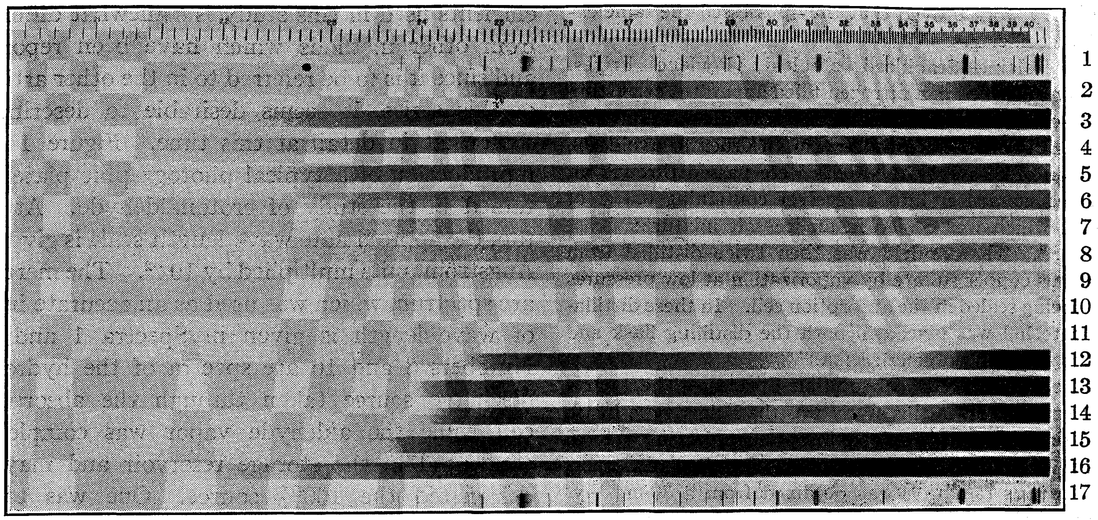

Fig. 1.—Reproduction of a typical spectrogram obtained in the study of crotonaldehyde.

(a) **Crotonaldehyde (Original).**—The crotonaldehyde obtained from the Niacet Chemical Corporation was purified by distillation through a 90-cm. Claisen-head column full of cut glass rings and equipped with a Hopkins condenser. The fraction boiling between 101–102° (750 mm.) was dried over anhydrous copper sulfate and redistilled in an atmosphere of nitrogen through a 30-cm. Vigreux column, b. p. 102.6–102.8°; d^{25}_4 0.8495; $n^{20}\text{D}$ 1.4356. Other drying agents such as calcium chloride and magnesium perchlorate caused more or less polymerization of the aldehyde.

(b) **Crotonaldehyde (Irradiated).**—One hundred cc. of the freshly distilled commercial crotonaldehyde, b. p. 101–102°, was placed in a Pyrex flask with 4 cc. of 6 *N* hydrochloric acid and exposed to strong sunlight for five hours. In some experiments the irradiated mixture was then treated with sodium bicarbonate and distilled through a 30-cm. Vigreux column. The water together with a small amount of aldehyde distilled between 90–95°. The temperature then rose rapidly and a chloride-free fraction was collected between 101.5–102.5°. This product was dried over anhydrous copper sulfate and distilled, b. p. 102.6–102.8°, $n^{20}\text{D}$ 1.4358. In other experiments the irradiated mixture was distilled at once; the large portion of the hydrochloric acid coming over in the first fraction, b. p. 90–101.5°. The main distillate, b. p. 101.5–102.5°, $n^{20}\text{D}$ 1.4356, was essentially chloride free. It was likewise dried and fractionated, b. p. 102.6–102.8°, $n^{20}\text{D}$ 1.4356. The crotonaldehyde samples prepared by both of these procedures are referred to as the "irradiated" sample since

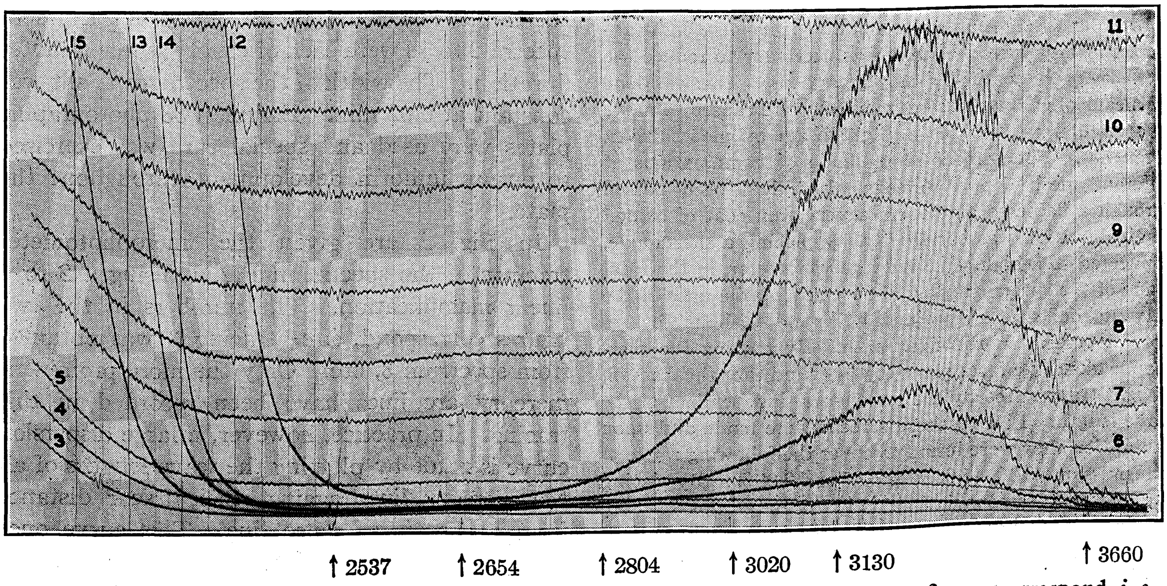

Fig. 2.—Microphotometer tracings of the spectra shown in Fig. 1. The numbers in the two figures correspond, *i. e.*, tracing 3 was obtained from spectrum 3, etc. The positions of the more prominent mercury arc lines are indicated.

preliminary work proved that they possessed the same extinction coefficients.

(c) **Acrolein.**—Stabilized acrolein (Poulenc Frères, Paris) was distilled in a nitrogen-filled apparatus consisting of a 90-cm. column, containing glass rings and equipped with a Hopkins reflux condenser. In order to avoid the formation of disacryl the vapors were passed through an ice-cooled condenser into a receiver containing 0.5 g. of catechol which was cooled in an ice–salt mixture; b. p. 53.0–53.2°. The acrolein was then twice distilled from anhydrous copper sulfate by vaporization at low pressures before being sealed in the absorption cell. In these distillations catechol was placed in both the distilling flask and receiver to avoid polymerization.

Method of Study of Absorption Spectra.—The quartz spectrograph used in this study was the Hilger type E316. It is primarily an ultraviolet instrument, having a focal plane of 18 cm. in length between λ 2000 and 4000 Å.

Continuous radiation was obtained from a 30-cm. hydrogen discharge between water-cooled iron electrodes. Purified hydrogen was pumped through the discharge tube at a constant rate during the exposures. The pressure in the tube was regulated by observing the structure of the discharge. A blue double herring bone structure was used since it is very sensitive to pressure change and also gives a source with the minimum number of lines due to atomic hydrogen.

The aldehyde vapors were studied in a fused silica absorption cell 40 cm. in length, 3 cm. in diameter and having plane parallel windows. A mercury manometer of 8 mm. inside diameter and a small reservoir for storing the liquid to be studied were connected to the tube by silica-to-Pyrex graded seals. The aldehyde was introduced into the reservoir in the following manner: the system was first flushed out with nitrogen and then about 3 cc. of the aldehyde was distilled at low pressure into the reservoir which contained 0.1 g. of catechol. While the reservoir was still cooled by means of solid carbon dioxide the system was evacuated, and sealed off.

In order to determine the amount of incident light absorbed at any wave length it was necessary to reduce the intensity of the source by known fractions. This was done by means of calibrated screens which were caused to move in a circular manner in the light beam by motor-driven eccentrics. The screens were made of combinations of different mesh copper screens which had been passed through a flame to give them a very thin coat of oxide.[3] The calibration was carried out by placing a thermopile, connected to a high sensitivity galvanometer, in the focal plane of the spectrograph and determining the ratio of the galvanic deflections obtained with and without the revolving screens in the light path. By moving the thermopile along the focal plane it was found that the fraction of light transmitted by the screens was independent of the wave length. Five of these screens were made and upon calibration they were found to cover the following range of transmission: 67.0, 45.0, 22.2, 5.85 and 2.90%. By placing the different screens individually or in groups of two, moving out of phase with one another, in the light path, a large variation in transmission could be obtained.

Since the method of obtaining extinction coefficients used in this study is somewhat different from other methods which have been reported and since it is to be referred to in the other articles of this series, it seems desirable to describe it somewhat in detail at this time. Figure 1 is a reproduction of a typical photographic plate obtained in the study of crotonaldehyde. At the top, the approximate wave length scale is given in Ångström units multiplied by 10^{-2}. The mercury arc spectrum which was used as an accurate index of wave length is given in Spectra 1 and 17. Numbers 3 and 16 are spectra of the hydrogen discharge source taken through the absorption cell while the aldehyde vapor was completely condensed in the storage reservoir and may be designated the 100% source. One was taken before and the other after all of the other spectra were taken in order to afford a check on the constancy of the source. If in any case it was found that the 100% source had changed in intensity during the time exposures were being made, the entire plate was discarded. Numbers 4, 5, 6, 7, 8, 9, 10 and 11 were taken in like manner except that rotating screens were placed in the path of light so that the intensity of the source was diminished, respectively, to 67, 45, 22.2, 14.9, 10.0, 5.85, 3.92 and 2.90% of the original intensity. Numbers 2, 12, 13, 14 and 15 are absorption spectra of crotonaldehyde taken with pressures in the cell of 42.5, 42.5, 12.0, 23.0 and 5.0 mm., respectively. These pressures were maintained by controlling the temperature of the liquid in the reservoir. Exposure times of spectra 2 to 16 were each of exactly three minutes duration. The width of the spectrograph slit was constant at 0.02 mm. Eastman 33 photographic plates were used and special care was exercised to ensure uniform development throughout the plate.

In Fig. 2 are given the microphotometer tracings of the spectra in Fig. 1, using a 2 to 1 linear magnification. The numbers in the two figures correspond, *i. e.*, tracing 3 was obtained from spectrum 3, etc. Only the more prominent mercury arc lines have been recorded in this tracing. In practice, however, a large dispersion curve is made by plotting the wave lengths of all the mercury lines against their linear distance from a chosen reference line. This curve once made may be used to determine the wave length of all points on any tracing having this 2 to 1 ratio to an original spectrogram. By placing the

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(3) G. R. Harrison, *J. Opt. Soc. Am.*, **18**, 492 (1929).

tracings on thin millimeter cross-section paper over a ground glass illuminating table, the linear distance of any point from the reference line may be obtained with sufficient accuracy to give the wave length in the ultraviolet to within one or two Ångström units.

In calculating ε, the molecular extinction coefficient, Lambert–Beer's law

$$\epsilon = \frac{l}{cl} \log \frac{I_0}{I} \tag{1}$$

is used in the form

$$\epsilon = \frac{RT}{pl}\left(2 - \log \frac{100\,I}{I_0}\right) \tag{2}$$

R is the gas constant in liter-atmospheres per mole per degree, T the absolute temperature, p the pressure of the gas in atmospheres, l the length in centimeters of the light beam in the absorbing medium, I_0 the intensity of the incident beam and I the intensity of the transmitted light. Since for a given spectrum T, p and l are measurable constants, it is obvious that wherever the ratio I/I_0 can be determined, ε may be calculated. In Fig. 2, tracings 3 to 11 inclusive are lines of known values of I/I_0. Hence wherever a tracing of an absorption spectrum crosses one of these lines the extinction coefficient may be determined. In regions of continuous absorption these points may be sufficient in number to give a satisfactory curve of extinction coefficients.

However, in regions of discontinuous absorption it is not always easy to estimate the point of intersection; furthermore, there are maxima and minima which do not strike any of the source tracings. To eliminate this difficulty an interpolation curve for a given wave length may be made by plotting log 100 I/I_0 against the perpendicular distance from an arbitrary base line. This gives a smooth curve and by measuring from this line the height of an absorption tracing at the wave length in question, log 100 I/I_0 may be obtained from the graph. For convenience a tracing representing zero transmission of the plate was used as the base line. In regions in which the source tracings are approximately horizontal, the same interpolation curve may be used for a considerable range of wave lengths. When this is not the case, a new curve must be plotted for each wave length at which extinction coefficients are desired. However, this is not a very tedious process since all curves have the same source values for log 100 I/I_0 and it is only necessary to read off the heights of the tracings and record them on the graph. The microphotometer used in this study has been described elsewhere and has been shown to have constant sensitivity and to give reproducible results.[4]

It may be recognized that because of overexposure between wave lengths 2450 and 2900 Å. and above 3600 Å., Figs. 1 and 2 are of no value in calculating extinction coefficients. In order to bring out these regions, some spectrograms were taken with the time of exposure reduced to sixty seconds, while still others had the spectrograph slit width reduced from 0.02 mm. to 0.01 mm. as well. As far as it could be ascertained, by studying overlapping regions, these variations had no effect upon the value of the extinction coefficients.

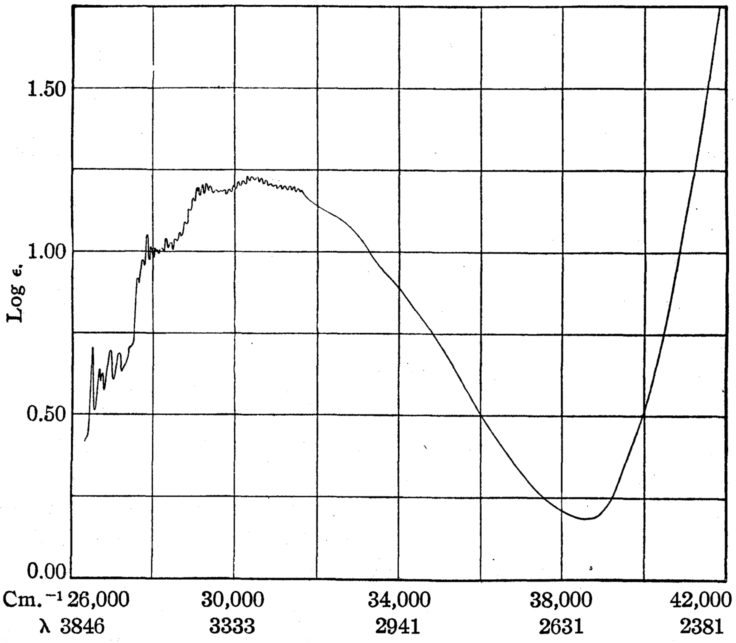

Fig. 3.—Logarithms of the molecular extinction coefficients of crotonaldehyde *vs.* wave numbers, cm.⁻¹ and wave lengths, λ, in Ångström units.

By using the method described above the extinction coefficients of crotonaldehyde and acrolein were obtained. These results are presented graphically in Figs. 3 and 4. As far as it is possible to make a comparison from the information available they are in general agreement

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[4] Leighton, Smith and Henson, *Rev. Sci. Instruments*, **5**, 431 (1934).

with those reported by Lüthy.[1c] It does not seem necessary to give detailed tables of extinction coefficients in addition to the results shown in the figures. However, in Table I are presented some typical results obtained in the comparison study of the original crotonaldehyde and the samples which were irradiated in the manner described above. It may be observed that within the limits of error both in regard to the measurement of wave lengths and the evaluation of the extinction coefficients, there is no difference between the two samples.

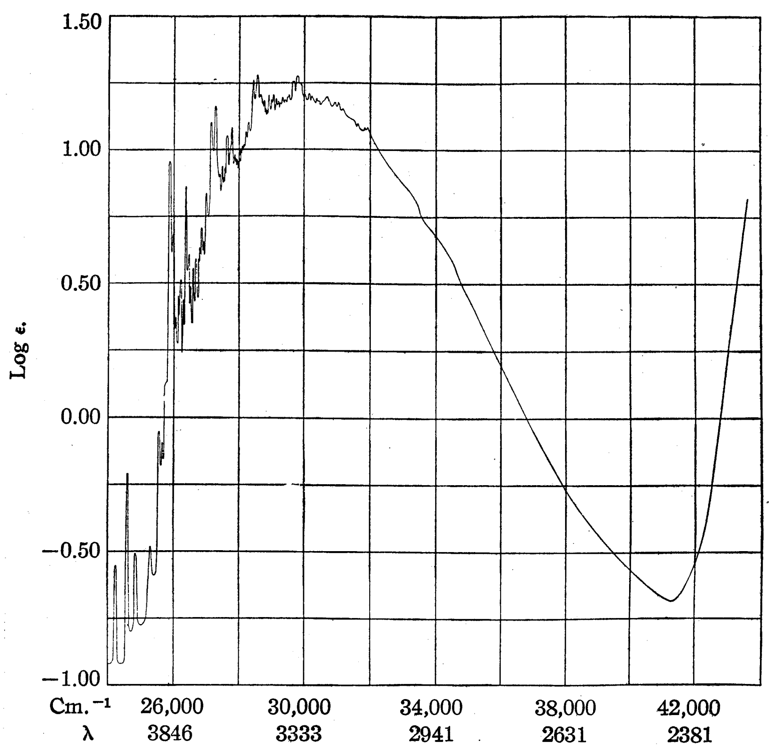

Fig. 4.—Logarithms of the molecular extinction coefficients of acrolein *vs.* wave numbers, cm.$^{-1}$ and wave lengths, λ, in Ångström units.

TABLE I

WAVE LENGTH AND LOG ε OF SOME CHARACTERISTIC ABSORPTION MAXIMA OF THE ORIGINAL AND THE IRRADIATED CROTONALDEHYDES

Wave length, Å. Original	Wave length, Å. Irradiated	Log ε Original	Log ε Irradiated	Difference in log ε of original and irradiated	Difference in log ε of two determinations on original
3588	3589	1.060	1.051	+0.009	+0.008
3529	3530	1.063	1.045	+ .018	− .005
3422	3423	1.216	1.219	− .003	+ .009
3411	3412	1.216	1.221	− .005	+ .009
3297	3299	1.244	1.233	+ .011	+ .011
			Average	.0060	.0064

Discussion of Results

Composition of Crotonaldehyde.—Crotonaldehyde is the starting material in the synthesis of many unsaturated compounds. In order to be sure of the configuration of these products it is of utmost importance to know the exact composition of the crotonaldehyde. The oxidation of both irradiated and non-irradiated aldehydes,[5] under conditions designed to avoid stereomutation, failed to show any evidence for the existence of the *cis* isomer or of vinylacetaldehyde in the original materials. However, there remained the possibility that the mere act of oxidation in the presence of resinous material, which is always formed, would give rise to only *trans*-crotonic acid even though the *cis* aldehyde was originally present. It was therefore desirable to study the composition of crotonaldehyde by a physical method such as the determination of absorption spectra. Although the absorption spectrum of crotonaldehyde has been reported by several investigators,[1b,c,e] the question of *cis–trans* isomerism has not been considered. Consequently, it seemed desirable to obtain extinction coefficients for both the original and irradiated crotonaldehydes. The procedure adopted for the preparation of the irradiated crotonaldehyde takes advantage of the possibility of both photochemical and thermal stereomutation in the presence of hydrochloric acid. Stereomutation of *cis*-crotonic acid by irradiation with sunlight has been reported by Wislicenus.[2a] Likewise stereomutation of *cis*-α-methylcrotonic acid during distillations at approximately 100° has been reported by Blaise[2b] and since corroborated.[6] It was found that during the thermal decomposition of α-methyl-α-hydroxybutyric acid and during the fractional distillation of the decomposition products, it was necessary to avoid even traces of hydrochloric acid in order to obtain a satisfactory yield of *cis*-α-methylcrotonic acid. If appreciable quantities of the catalyst were present only the *trans* isomer could be isolated.

A comparison of results, Table I, indicates that both the extinction coefficients and wave lengths

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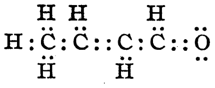
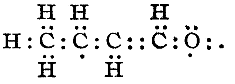
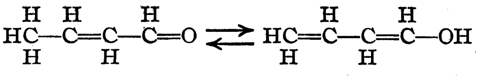
(5) Young, THIS JOURNAL, **54**, 2498 (1932).

(6) Young, Dillon and Lucas, *ibid.*, **51**, 2529 (1929).

of characteristic maxima agree within experimental error for both the original and irradiated samples. If the original aldehyde contained an appreciable quantity of the *cis* isomer and the concentration of this isomer were changed by the method adopted, one might expect a shift in the wave length of the characteristic peaks, thus causing a twinning effect or the appearance of small peaks between the larger ones. Likewise, a difference in extinction coefficients might be expected. Since these differences do not appear, it may be reasoned that commercial crotonaldehyde is essentially the pure *trans* isomer just as the oxidation experiments had indicated.[5] It should be noted that several papers[7] have appeared on the Raman spectra of crotonaldehyde. However, only Gredy and Piaux reported lines which were attributed to traces of the *cis* isomer. Two possible explanations may be suggested to account for the apparent lack of the unstable stereoisomer in crotonaldehyde. One is the occurrence of resonance between the forms  $\mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\mathrm{C}}}}:\overset{\mathrm{H}}{\ddot{\mathrm{C}}}::\underset{\mathrm{H}}{\mathrm{C}}:\overset{\mathrm{H}}{\ddot{\mathrm{C}}}::\ddot{\mathrm{O}}$ and  $\mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\mathrm{C}}}}:\overset{\mathrm{H}}{\dot{\mathrm{C}}}:\underset{\mathrm{H}}{\mathrm{C}}::\overset{\mathrm{H}}{\ddot{\mathrm{C}}}:\ddot{\mathrm{O}}:.$ A second explanation is that crotonaldehyde may consist of a tautomeric system of high mobility.



$$\underset{\mathrm{I}}{\mathrm{H\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{=}\underset{H}{C}{-}\overset{H}{C}{=}O}} \rightleftarrows \underset{\mathrm{II}}{\mathrm{H\overset{H}{C}{=}\underset{H}{C}{-}\overset{H}{C}{=}\underset{H}{C}{-}OH}}$$

I II

The aldehyde group is known to be one of the most efficient groups in activating a prototropic system.[8] The third possible tautomer, vinylacetaldehyde, would not be expected since there is no substitution in the γ-position.[9]

Comparison of Absorption Spectra of Crotonaldehyde and Acrolein.—By an inspection of Figs. 3 and 4, similarities and differences between the absorption spectra of crotonaldehyde and acrolein become obvious. Apparently the fundamental absorption processes are the same in the two compounds and the differences in the spectra result from the variation in length of the carbon chain.

Although the values of log ϵ obtained from different spectrograms varied by about 2% in regions of strong absorption by the vapor, the relative values at successive wave lengths can be obtained quite accurately and hence all of the small peaks and valleys appearing in these figures do exist. That is to say, two absorption curves obtained independently have the same characteristic shapes but one may lie above or below the other. Log ϵ values for all points of inflection shown for both aldehydes are the average values obtained from two or more spectrograms and from two or more pressures recorded on each of these. It was found that extinction coefficients calculated for crotonaldehyde from spectrograms of saturated vapor (42.5 mm. or less) were in substantial agreement with values obtained at lower pressures, indicating that deviations from the perfect gas law were not appreciable under these conditions. For acrolein the pressures used were well below the saturation value. They ranged between 30 and 150 mm. Over this range the values of ϵ reported for the maxima and minima of the discontinuous region are independent of pressure.

The generally accepted interpretation of discontinuous absorption is that the primary act of absorption produces only activated molecules, while, on the other hand, a continuum is thought to signify that dissociation occurs in the primary process. In Fig. 2 it may be observed that the strong lines of the mercury arc are well distributed among the continuous and discontinuous regions of absorption shown by crotonaldehyde. Hence, this aldehyde, as well as acrolein, if studied with the aid of a quartz mercury arc and monochromator, appears to offer an excellent opportunity to correlate these spectral interpretations with photochemical results. Do polymerization or decomposition processes occur in both regions of absorption and, if so, is there a marked change in the quantum yields of these reactions as the studies are shifted from the discontinuous to continuous regions? These questions and related ones are being studied at the present time in this Laboratory.

The authors are indebted to Professor P. A. Leighton for helpful suggestions in regard to this study and for the use of the microphotometer of Stanford University. Substantial aid has been received from Mr. Darrell Osborne in the compilation of experimental data. Likewise, the authors wish to express their appreciation for grants-in-aid from the National Research Council

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[7] (a) Hibben, *Proc. Nat. Acad. Sci.*, **18**, 532 (1932); (b) Gredy and Piaux, *Compt. rend.*, **198**, 1235 (1934); *Bull. soc. chim.*, [5] **1**, 148 (1934).

[8] Baker, "Tautomerism," D. Van Nostrand Company, Inc., New York, N. Y., pp. 44–45.

[9] Ingold, "Annual Reports on the Progress of Chemistry," **24**, 111 (1927).

and the Board of Research of the University of California.

Summary

A modified procedure for obtaining molecular extinction coefficients has been described.

Working with the vapor phase, the ultraviolet absorption spectra of crotonaldehyde and acrolein have been determined quantitatively.

Experiments designed to test for the presence of *cis*-crotonaldehyde in the commercial product gave results which indicate that this form of the aldehyde was not present.

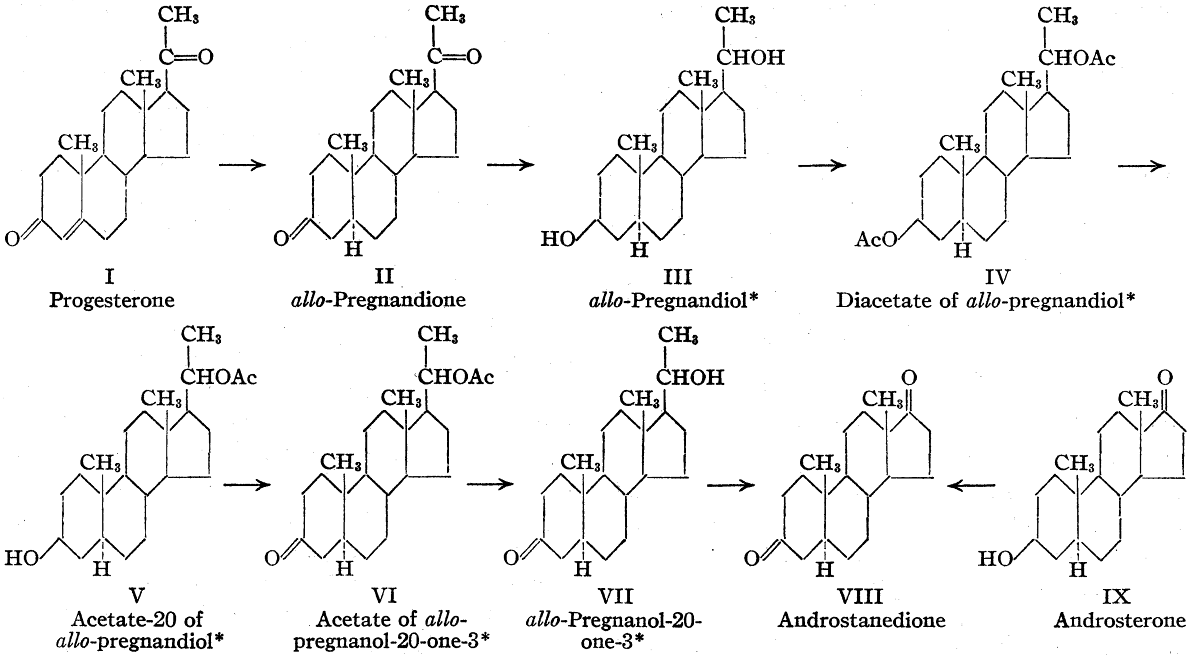
LOS ANGELES, CALIF. RECEIVED SEPTEMBER 30, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE PARKE, DAVIS & CO. RESEARCH LABORATORIES]

Sterols. VIII. Preparation of Androstanedione from *allo*-Pregnandiol

BY RUSSELL E. MARKER, OLIVER KAMM, DAVID M. JONES AND THOMAS S. OAKWOOD

The present paper serves to establish a complete structural relationship between the female sex hormone, progesterone (I) and the male sex hormone, androsterone (IX). This has been accomplished by supplementing the known preparation[1] of androstanedione (VIII) by oxidation of androsterone, with a new method of preparation of the same compound starting with *allo*-pregnandione (II). The last mentioned compound has been described previously by Butenandt,[2] who obtained it by reducing progesterone to a mixture of pregnandiol and *allo*-pregnandiol, oxidizing the mixture, and separating from it pregnandione and *allo*-pregnandione. The reactions involved in our work are illustrated by formulas II–VIII.



I Progesterone

II *allo*-Pregnandione

III *allo*-Pregnandiol*

IV Diacetate of *allo*-pregnandiol*

V Acetate-20 of *allo*-pregnandiol*

VI Acetate of *allo*-pregnanol-20-one-3*

VII *allo*-Pregnanol-20-one-3*

VIII Androstanedione

IX Androsterone

* The designation *trans* has been omitted at the suggestion of the referee. It seems to us, however, that such a designation is needed to differentiate our new compounds from previously known isomers.

allo-Pregnandione (II) was obtained by oxidation with chromic anhydride of the mixture of pregnandiol and *allo*-pregnandiol obtained from concentrates of human pregnancy urine. Crystallization from acetone gave pure *allo*-pregnandione. The latter was reduced in acetic acid at room temperature with platinum oxide and hydrogen to *allo*-pregnandiol (III). This gave a digitonide readily. The diol was converted to the diacetate (IV). The acetyl group in the 3-

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(1) Butenandt and Tscherning, *Z. physiol. Chem.*, **229**, 189 (1934).

(2) Butenandt and Fleischer, *Ber.*, **68**, 2094 (1935).

position was then hydrolyzed with potassium hydroxide in methyl alcohol solution at 15–20°, giving the 3-hydroxy-20-acetoxy compound (V). The 3-hydroxy group was then oxidized to a keto group to give Compound VI. Hydrolysis of the acetyl group at position 20 resulted in *allo*-pregnanol-20-one-3 (VII).

The conversion of the ol-one (VII) to androstanedione was carried out without isolation of the intermediate compounds. The ol-one was dehydrated by heating in acetic acid with anhydrous zinc chloride. The product was freed of acetic acid and the chloride was dissolved in chloroform and ozonized. The ozonide was decomposed by heating with acetic acid. The neutral fraction yielded two products, one a high-melting material of undetermined constitution, and the other androstanedione melting at 126-128°. This was found to be identical with androstanedione obtained by the oxidation of androsterone.

Experimental

allo-**Pregnandione.**—A solution of 50 g. of pregnandiol-*allo*-pregnandiol mixture in 3500 cc. of glacial acetic acid was cooled to 10° and treated with a solution of 50 g. of chromic anhydride in 600 cc. of 90% acetic acid, added over a period of four hours. The resulting mixture was allowed to stand overnight at room temperature, when 100 cc. of methyl alcohol was added and the acetic acid removed under reduced pressure. The residue was extracted with ether and the ether solution washed successively with dilute hydrochloric acid, water, 10% sodium bicarbonate solution, and finally again with water. The ether was then evaporated, giving 45 g. of oily white solid. This was dissolved in 190 cc. of boiling acetone, the solution cooled to 0°, and allowed to stand for twelve hours. The precipitate of *allo*-pregnandione was filtered off, washed with a small amount of acetone, and recrystallized from acetone. Its melting point was found to be 199–200°. The mother liquors contained the isomeric pregnandione.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.7; H, 10.2. Found: C, 79.4; H, 10.3.

allo-**Pregnandiol.**—To a solution of 3 g. of *allo*-pregnandione in 100 cc. of glacial acetic acid was added 2 g. of platinum oxide. The mixture was shaken with hydrogen at 45 pounds (3 atm.) pressure during seventy-five minutes, the catalyst filtered off, and the acetic acid concentrated under reduced pressure. The residue was crystallized from ethyl alcohol. Its melting point was 195–196°.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.7; H, 11.3. Found: C, 78.8; H, 11.4.

allo-**Pregnandiol Diacetate.**—A solution of 300 mg. of *allo*-pregnandiol in 2 cc. of acetic anhydride was refluxed during two hours. The reaction product which solidified on cooling was taken up with water and filtered. After crystallization first from ethyl alcohol and then from ethyl acetate it melted at 142–143°.

Anal. Calcd. for $C_{25}H_{40}O_4$: C, 74.2; H, 10.0. Found: C, 74.2; H, 10.1.

allo-**Pregnandiol Monoacetate.**—To a solution of 1.55 g. of the diacetate in 375 cc. of methyl alcohol was added 28.3 cc. of a methyl alcohol–potassium hydroxide solution containing 0.0062 g. of potassium hydroxide per cc. The mixture was kept at 15–20° for forty-two hours. It was then neutralized with dilute hydrochloric acid and evaporated to a small volume. Water was added and the product filtered. After crystallization from petroleum ether it melted at 170–171°.

Anal. Calcd. for $C_{23}H_{38}O_3$: C, 76.2; H, 10.6. Found: C, 76.3; H, 10.7.

Acetate of *allo*-Pregnanol-20-one-3.—To a solution of 360 mg. of the monoacetate of *allo*-pregnandiol in 25 cc. of acetic acid was added 100 mg. of chromic anhydride in acetic acid. The solution was kept at room temperature for sixteen hours after which methyl alcohol was added and the acetic acid removed under reduced pressure. Water was added and the product filtered off. After crystallization from ethyl alcohol and finally from petroleum ether it melted at 156°.

Anal. Calcd. for $C_{23}H_{36}O_3$: C, 76.6; H, 10.1. Found: C, 76.5; H, 10.1.

allo-**Pregnanol-20-one-3.**—A solution of 180 mg. of the acetate of *allo*-pregnanol-20-one-3 in ethyl alcohol was treated with an excess of potassium hydroxide solution and refluxed during two hours. The solution was neutralized with hydrochloric acid and concentrated under reduced pressure. Water was added and the solid filtered off and crystallized from dilute ethyl alcohol when it showed a melting point of 195°.

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.7. Found: C, 79.4; H, 10.8.

Androstanedione.—To a solution of 500 mg. of *allo*-pregnanol-20-one-3 in 8 cc. of glacial acetic acid was added 500 mg. of freshly fused zinc chloride. The solution was refluxed for three hours, cooled, and diluted with water. A semi-solid precipitate separated which after standing overnight was filtered off. It was dissolved in 100 cc. of chloroform and ozone was passed into the solution during thirty minutes at 0° at the rate of 7 liters of ozone per hour. The chloroform was evaporated at 25° and the residue taken up in 100 cc. of glacial acetic acid and heated on a steam-bath during one hour. The solution was then cooled to room temperature and 100 mg. of chromic anhydride added. After thirty minutes, methyl alcohol was added, the solvents evaporated at 40° and the residue dissolved in 50 cc. of water and 50 cc. of ether. The ether solution was separated, washed with 5% sodium hydroxide to free it of organic acids, and evaporated to dryness. The residue upon sublimation in a high vacuum yielded two fractions. The higher fraction gave a material melting at 185°. The lower fraction was resublimed at 110°, and then crystallized from acetone. The yield was 40 mg. of a product melting at 128°.

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.1; H, 9.8. Found: C, 78.4; H, 9.9.

Oxidation of Androsterone.—To a solution of 335 mg. of androsterone in 120 cc. of acetic acid was added 116 mg. of chromic oxide. This was kept at 15–20° for thirteen hours and then at 25–30° for eight hours. Methyl alcohol was added and the solvents evaporated under reduced pressure. Water was added and the precipitate crystallized from acetone. It melted at 132°.

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.1; H, 9.8. Found: C, 79.3; H, 9.7.

A mixture of the two samples of androstandione gave a melting point of 128–129°.

Summary

allo-Pregnandiol, a reduction product of progesterone, was converted into androstanedione, an oxidation product of androsterone, thus establishing a complete structural relationship between the female sex hormone, progesterone, and the male sex hormone, androsterone.

STATE COLLEGE, PA.
DETROIT, MICH.
RECEIVED OCTOBER 10, 1936

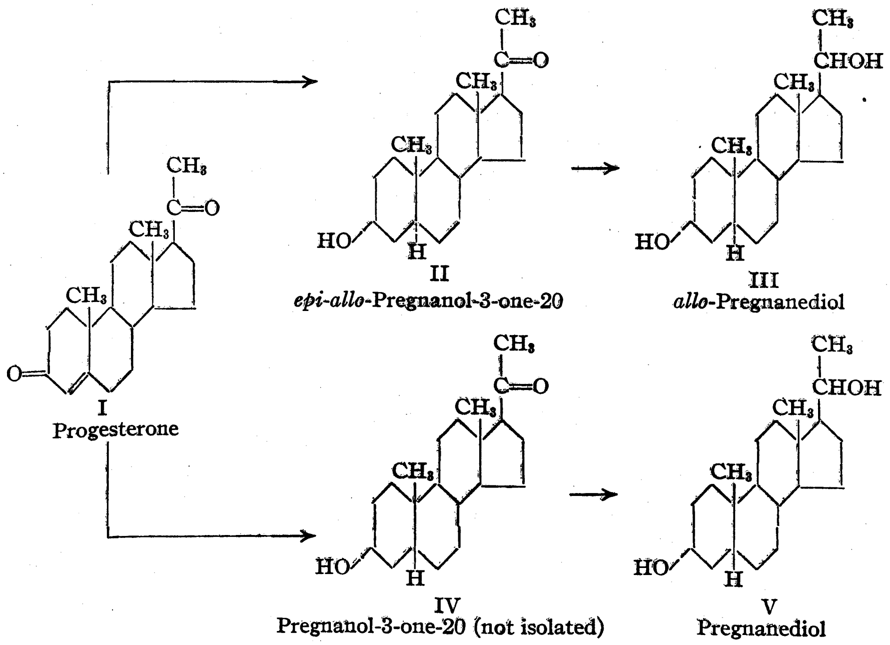
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE, AND THE PARKE, DAVIS & COMPANY RESEARCH LABORATORIES]

Sterols. IX. Isolation of *epi*-Pregnanol-3-one-20 from Human Pregnancy Urine

BY RUSSELL E. MARKER, OLIVER KAMM AND RALPH V. MCGREW

A reinvestigation of the sterol derivatives contained in human pregnancy urine fails to show the presence of progesterone. Since our experiments were conducted on a large scale using the sterol fraction from 10,000 gallons of human pregnancy urine, it seems reasonable to conclude that the corpus luteum hormone is not excreted as such by the human subject during pregnancy. Whether or not the *normal* female excretes the hormone is the subject of an investigation now in progress.

It is known that the neutral carbinol fraction from human pregnancy urine consists mainly of a mixture of pregnanediol and *allo*-pregnanediol, which differ only in the configuration of rings A and B of the sterol nucleus. We have now found, however, that sterols which may be considered as reduction products intermediate between progesterone and the pregnanediols *are* eliminated. In this article we describe the isolation of a compound of that type, namely, a pregnanolone.


I
Progesterone

II
epi-allo-Pregnanol-3-one-20

III
allo-Pregnanediol

IV
Pregnanol-3-one-20 (not isolated)

V
Pregnanediol

Butenandt[1] in the isolation of progesterone from hog corpora lutea obtained *allo*-pregnanol-3-one-20 melting at *195°* which he prepared later by the degradation of stigmasterol. Since stigmasterol possesses the normal arrangement (of cholesterol) in respect to the hydroxyl group and since his method of synthesis did not produce an inversion of this group, the naturally occurring allopregnanolone also has the hydroxyl group in the normal arrangement.

The epimeric form of *allo*-pregnanol-3-one-20 has been obtained from the residues of human pregnancy urine after removal of the theelin, theelol and other known sterol derivatives. It is present in quantities of 1-2 mg. per gallon of urine. This product does not absorb bromine

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[1] Butenandt and co-workers, *Ber.*, **67**, 1441, 1897 (1934).

and is not precipitated by digitonin. Upon oxidation it yields *allo*-pregnanedione and upon reduction, *allo*-pregnanediol-3,20. The formula of the new compound and its relationship to other sterol derivatives are represented herewith.

In our study of the sterol residues from human pregnancy urine it was found that the major portion consisted of carbinols together with some ketosterols. The carbinols were separated from the non-carbinol material by means of the sodium salts of their half esters with phthalic acid. The ketonic carbinols were then separated from the plain carbinols through the water soluble betaine hydrazones. The ketonic carbinols were then further separated by crystallization of their semicarbazones. The non-carbinol fraction gave practically no ketones when treated with the betaine hydrazine reagent, thus demonstrating the absence of progesterone in these residues.

Experimental

Separation of Carbinols from Hydrocarbons.—The residue from 10,000 gallons of human pregnancy urine after the separation of theelin and theelol by the Doisy method[2] was hydrolyzed by refluxing with an excess of alkali. This was then steam distilled until no more volatile oils came over. The residue was cooled, filtered, the solid precipitate washed well with water, dried and finally shaken with ice-cold ether. The ether-insoluble portion consists of a mixture of pregnanediol and *allo*-pregnanediol.

The ether-soluble portion was concentrated, leaving 777 g. of tarry residue. This was dissolved in benzene and the carbinols present converted into their acid phthalates according to the following procedure. To 50 g. of the tar was added 25 g. of phthalic anhydride and 25 cc. of dry pyridine. The solution was heated on a steam-bath for two hours, ether was added and the pyridine removed by washing with dilute sulfuric acid. The ether solution was shaken with a solution of 50 g. of sodium carbonate in 200 cc. of water. The ether layer contained the non-carbinol fraction. The carbonate solution, which was extracted thoroughly with ether, was acidified with sulfuric acid and then again extracted with ether. The ether was evaporated and the phthalates saponified by refluxing for two hours with 200 cc. of alcohol containing 50 g. of potassium hydroxide in 40 cc. of water. Water was added and the alcohol distilled. The alkaline solution with its suspended solids was extracted with ether and thus yielded 31.4 g. of a carbinol fraction.

Separation of Ketonic Carbinols from Carbinol Fraction.—To 31.4 g. of total carbinols was added 30 cc. of ethyl alcohol and 5 g. of betaine hydrazine chloride. The reaction mixture was boiled for fifteen minutes on a steam-bath, poured into 200 cc. of water containing ice and the solution thoroughly extracted with ether. The ether layer contained the non-ketonic carbinols, whereas the aqueous layer contained the ketonic carbinols. An excess of hydrochloric acid was added to the aqueous layer and the solution warmed on a steam-bath. The oil which separated was extracted with ether. This gave 2.0 g. of ketonic carbinols. The total urine residue gave 31 g. of ketonic carbinols.

Semicarbazone of *epi-allo*-Pregnanol-3-one-20.—Thirty-one grams of the ketonic carbinol fraction was sublimed in 3-g. quantities in high vacuum, collecting the portion from 140–200° which weighed 23 g. To a solution of 8 g. of the sublimate in 100 cc. of alcohol was added 13.6 g. of sodium acetate and 11.1 g. of semicarbazide hydrochloride. The alcohol was distilled to dryness and the semicarbazone residue washed with hot water and finally with ether. The white solid (7.3 g.) was crystallized from alcohol to a constant melting point of 248–250°, dec.

Anal. Calcd. for $C_{22}H_{37}N_3O_2$: C, 70.3; H, 9.9. Found: C, 69.9; H, 9.9.

***epi-allo*-Pregnanol-3-one-20.**—To a solution of 3 g. of semicarbazone in 150 cc. of alcohol was added 15 cc. of sulfuric acid in 30 cc. of water. The product was refluxed for one-half hour, poured into water and thoroughly extracted with ether. The ether was distilled and the residue sublimed in high vacuum at 130°. The sublimate was crystallized from 70% alcohol and then from 70% acetone, m. p. 162–164°. It does not absorb bromine in the cold, and does not precipitate with digitonin; $[\alpha]^{30}D$ +91.0°, $c = 1\%$ in alcohol.

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.8. Found: C, 79.3; H, 10.8.

Oxidation of *epi-allo*-Pregnanol-3-one-20 to *allo*-Pregnanedione.—To a solution of 180 mg. of *epi-allo*-pregnanol-3-one-20 in 16 cc. of glacial acetic acid was added 58 mg. of chromic anhydride in 30 cc. of 90% acetic acid. After standing for sixteen hours at 15–20° the solution was diluted with water and the precipitate was collected, dried and sublimed in high vacuum at 115°. The sublimate after crystallization from acetone melted at 198–200° and did not depress the melting point of *allo*-pregnanedione (m. p. 200°).

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.7; H, 10.2. Found: C, 79.5; H, 10.1.

Acetate of *epi-allo*-Pregnanol-3-one-20.—To 1 g. of *epi-allo*-pregnanol-3-one-20 was added 5 cc. of acetic anhydride. The mixture was refluxed for thirty minutes and the excess acetic anhydride distilled under reduced pressure. The residue was sublimed at 130° with a mercury vapor pump. It was crystallized from 70% alcohol and then from 70% acetone, m. p. 139–140°; $[\alpha]^{30}D$ +112°, $c = 1$ g. per 100 cc. in alcohol.

Anal. Calcd. for $C_{23}H_{36}O_3$: C, 76.8; H, 10.1. Found: C, 77.0; H, 10.0.

3 - *epi* - *allo* - Pregnanediol - 20 - trans.—*epi* - *allo* - Pregnanol-3-one-20 (100 mg.) was hydrogenated in acetic acid solution (100 cc.) using platinum oxide (100 mg.) at a pressure of 45 lb. (3 atm.). The catalyst was filtered off and the acetic acid distilled under reduced pressure. The residue was crystallized from acetone which yielded a product melting at 205–207°. Mixed with *allo*-pregnanediol (m. p. 242°) it gave a depression in melting point to 194°.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.8; H, 11.3. Found: C, 78.8; H, 11.2.

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(2) Doisy, *et al.*, *J. Biol. Chem.*, **87**, 357 (1930).

Diacetate of 3-*epi-allo*-Pregnanediol-20-*trans*.—A solution of 100 mg. of 3-*epi-allo*-pregnanediol-20-*trans* in 5 cc. of acetic anhydride was refluxed for one hour. The acetic anhydride was evaporated under reduced pressure and the residue recrystallized from 60% acetone. Its melting point was found to be 124°.

Anal. Calcd. for $C_{25}H_{40}O_4$: C, 74.4; H, 10.0. Found: C, 74.5; H, 10.2.

Discussion

Although the human corpus luteum contains only traces of progestin,[3] the quantity being so small that it is difficult to imagine that it can be of great significance in the maintenance of pregnancy, it has been demonstrated recently[4] that during pregnancy the placenta may produce its own progestin.

The new sterol that we have isolated, *epi-allo*-pregnanol-3-one-20, probably represents the first stage of the reduction in the body of progesterone to *allo*-pregnanediol; at any rate, it seems logical to expect that the conjugated ketone system would be the easier to reduce, giving as the first reduction products pregnanolone and *allo*-pregnanolone, which on further reduction yield the pregnanediols. So far we have succeeded in isolating only one isomer of pregnanolone (II), but we have evidence that the one represented by formula IV is present also in urine residues.

From our present knowledge of the sterols it is apparent that the utilization of the sterol sex hormones by the body in performing their functions as sex hormones is accompanied by oxidation and reduction reactions. This is shown by the fact that testosterone, which occurs in the testes, after performing its duty as a sex hormone, is eliminated in male urine as its reduction products, of which dehydro-iso-androsterone and androsterone so far have been isolated. In the case of progesterone which functions as a hormone during pregnancy, the products which are eliminated from the body also are its reduction products, the pregnanolones and the pregnanediols. It may be significant that pregnancy urine contains no progesterone.

During pregnancy theelin and theelol are eliminated in the form of their conjugation products with glucuronic acid. The fact that very little theelin is found in the urine of the non-pregnant female who uses it as a hormone would also suggest that theelin may be thrown off from the normal animal in a more extensively altered form just as in the stallion the male sex hormone is eliminated as a theelin conjugate. There is a possibility, therefore, that unchanged progesterone may be obtained from non-pregnancy female urine. The physiological action of the sex hormones, therefore, appears to be chemical as well as physical.

Summary

epi-allo-Pregnanol-3-one-20, a new ketonic sterol, was isolated from human pregnancy urine. This on oxidation gave *allo*-pregnanedione. Catalytic reduction gave *allo*-pregnanediol-3-(*cis*)-20(*trans*). The acetates of these compounds are described.

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[3] J. P. Pratt, *Arch. Path.*, **19**, 381 (1935).

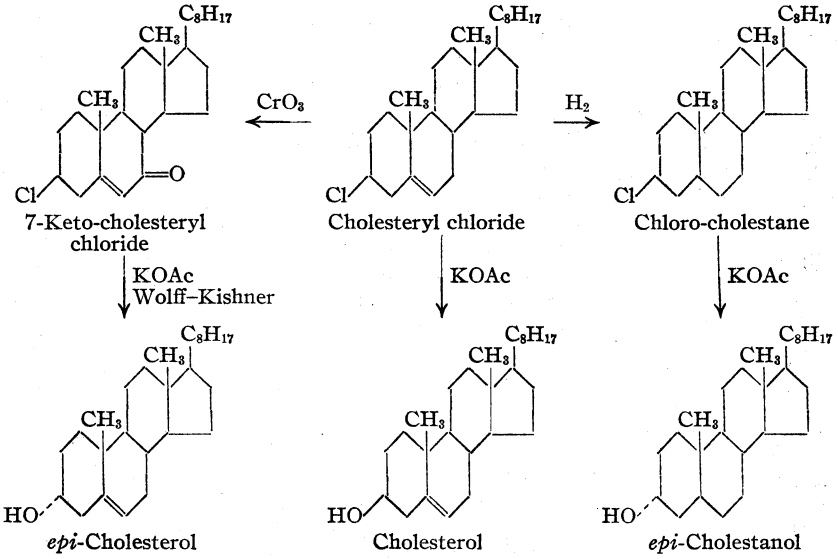
[4] McGinty, McCullough and Wolter, *Proc. Soc. Exptl. Biol. Med.*, **34**, 176 (1936).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE PARKE, DAVIS & CO. RESEARCH LABORATORIES]

Sterols. X. Cholesterol Derivatives

BY RUSSELL E. MARKER, OLIVER KAMM, GEORGE H. FLEMING, ALEXANDER H. POPKIN AND EUGENE L. WITTLE

In our studies on sterols we have prepared a number of derivatives substituted in ring B. On the oxidation of cholesteryl chloride by chromic oxide in acetic acid, 7-keto-cholesteryl chloride can be isolated in yields of 25%. When this is treated with potassium acetate it gives a mixture of 7-keto-cholesterylene and the acetate of 7-keto-*epi*-cholesterol. The latter when reduced by the Wolff–Kishner method gives *epi*-cholesterol, which is identical with *epi*-cholesterol previously prepared by us.[1]



When cholesteryl chloride is hydrolyzed it gives a compound with the hydroxyl group in the normal (cholesterol) arrangement. However, if the double bond is first reduced to cholestyl chloride and this product is hydrolyzed a Walden inversion occurs leading to an epimeric hydroxyl group. The same is true when 7-keto-cholesteryl chloride is hydrolyzed, giving an epimeric -OH group. This is very unusual in view of the fact that the double bond in both compounds is in the same position. It was noticed that cholesteryl chloride is hydrolyzed readily with potassium acetate in boiling acetic acid whereas with the other two compounds it was necessary to heat to 180° for hydrolysis.

When 7-keto-cholesteryl chloride is reduced by platinum oxide in acetic acid it gives a mixture of 7-hydroxycholestyl chloride and α-cholestyl chloride, the ketonic group of a portion of the material being reduced to a methylene group. Aluminum isopropylate and 7-keto-cholesteryl chloride give 7-hydroxycholesteryl chloride. When the latter compound is reduced by platinum oxide in acetic acid it also gives a mixture of 7-hydroxycholestyl chloride and α-cholestyl chloride in about equal portions. 7-Hydroxycholestyl chloride, on reduction with sodium in amyl alcohol, gives 7-hydroxycholestane. The -OH group of both compounds may readily be oxidized to give the corresponding ketones.

Experimental

7-Keto-cholesteryl Chloride.—To a solution of 203 g. of cholesteryl chloride in 3500 cc. of acetic acid kept at 55° there was added with stirring over a period of one hour a solution of 150 g. of chromic oxide in 100 cc. of water and 100 cc. of glacial acetic acid. Stirring was continued during an additional two hours. Ethyl alcohol was added and the reaction mixture was concentrated under reduced pressure at 55° to a volume of 1.5 liters. To this was added 100 cc. of water and the mixture was cooled overnight. The crystalline material was filtered, washed with 600 cc. of alcohol followed by 300 cc. of acetone and finally was recrystallized from acetone. The yield was 50 g. of a product melting at 145°. The melting point of the semicarbazone was 176°.

Anal. Calcd. for $C_{27}H_{43}OCl$: C, 77.4; H, 10.3. Found: C, 77.8; H, 10.2. *Anal.* Calcd. for $C_{28}H_{46}OClN_3$: C, 70.7; H, 9.7. Found: C, 70.5; H, 10.0.

***epi*-Cholesterol from 7-Keto-cholesteryl Chloride.**—To a solution of 5 g. of 7-keto-cholesteryl chloride in 25 cc. of valeric acid, 7 g. of fused potassium acetate was added and the mixture was refluxed for fourteen hours. The reaction mixture was extracted with ether, and the ether solution washed with sodium carbonate solution. The acetate obtained after evaporation of the ether was hydrolyzed by means of alcoholic potassium hydroxide. The resulting oily material was dried and treated with 2 g. of succinic

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(1) Marker, Oakwood and Crooks, THIS JOURNAL, **58**, 481 (1936).

anhydride in 15 cc. of pyridine, being heated four hours on the steam-bath. The reaction product was dissolved in ether and washed free of pyridine with hydrochloric acid. The succinate was then removed from ether by washing with sodium carbonate solution, the resulting solution being again washed with ether. [The ether solutions were worked up in a later experiment to give 7-keto-cholesterylene.] The alkaline solution was acidified and extracted with ether to remove the succinate, which was then hydrolyzed by boiling with alcoholic potassium hydroxide. The resulting product was then converted to the semicarbazone by heating with alcoholic semicarbazide acetate. This crude product was added directly to 10 cc. of absolute alcohol and to this was added a solution of 0.2 g. of sodium in 10 cc. of absolute alcohol. This was heated at 170–180° for six hours after which water was added and the product extracted with ether. The product was then sublimed at 140° using a mercury vapor pump and the sublimate crystallized from alcohol. Its melting point was 141°. Mixed with cholesterol (m. p. 147°) it gave a depression in melting point of 9°. Mixed with known *epi*-cholesterol it gave no depression.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.9; H, 12.0. Found: C, 84.0; H, 11.8.

7-Keto-cholesterylene.—To 1 g. of 7-keto-cholesteryl chloride dissolved in 30 cc. of alcohol was added 1.5 g. of potassium hydroxide in 2 cc. of water. The solution was refluxed two hours. Water was added and the product extracted with ether. After crystallization from alcohol it melted at 114°.

Anal. Calcd. for $C_{27}H_{42}O$: C, 84.8; H, 10.9. Found: C, 84.4; H, 10.8.

The same product was obtained as a by-product in the preparation of *epi*-cholesterol from 7-keto-cholesteryl chloride.

Reduction of 7-Keto-cholesteryl Chloride with Platinum Oxide Catalyst.—To a solution of 5 g. of 7-keto-cholesteryl chloride dissolved in 200 cc. of glacial acetic acid was added 1.5 g. of platinum oxide. The mixture was shaken with hydrogen under a pressure of 45 pounds (3 atm.) for six hours when the catalyst was filtered off and the acetic acid distilled under reduced pressure. The residue after crystallization from alcohol melted at 114.5°. Mixed with α-cholestyl chloride (m. p. 114°) it gave no depression in melting point.

Anal. Calcd. for $C_{27}H_{47}Cl$: C, 79.6; H, 11.6. Found: C, 79.6; H, 11.6.

The mother liquors from the above reduction contained about 80% of a product which would not crystallize and which was not cholestyl chloride since that product is almost completely insoluble in cold alcohol. The subsequent experiments showed that these mother liquors contained 7-hydroxycholestyl chloride.

7-Keto-cholestyl Chloride.—The solvent from the mother liquors in the previous experiment was evaporated. To 2 g. of the residue was added 20 cc. of acetic acid and a solution of 0.7 g. of chromic oxide in 3.4 cc. of acetic acid. The reaction mass was kept at 50–60° for two hours, then allowed to stand overnight at room temperature. A crystalline product separated and was filtered off and recrystallized from alcohol. Its melting point was 139°.

Anal. Calcd. for $C_{27}H_{45}OCl$: C, 77.1; H, 10.7. Found: C, 77.1; H, 10.6.

Cholestanol-7.—To 6 g. of crude 7-hydroxycholestyl chloride in 175 cc. of dry boiling amyl alcohol was added 12.5 g. of sodium. When the reaction was complete water was added and the alcoholic layer was separated and evaporated under reduced pressure. The residue crystallized from alcohol in needles melting at 117.5°.

Anal. Calcd. for $C_{27}H_{48}O$: C, 83.5; H, 12.4. Found: C, 83.4; H, 12.3.

Cholestanone-7.—To a solution of 2 g. of 7-hydroxycholestane in 35 cc. of acetic acid was added 0.7 g. of chromic oxide in 4 cc. of acetic acid. The product was kept at 50° for four hours and allowed to stand at room temperature for an additional twenty-four hours. Water was then added and the oxidation product extracted with ether. The ether solution was washed with sodium carbonate solution, the ether evaporated and the residue crystallized from acetone. Its melting point was observed to be 117° which is the same as that of 7-hydroxycholestane; mixed with that product, however, it showed a depression of 10°.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.9; H, 12.0. Found: C, 84.3; H, 12.1.

7-Hydroxycholesteryl Chloride.—To a solution of 40 g. of 7-keto-cholesteryl chloride (m. p. 145°) in 510 cc. of dry isopropyl alcohol was added 30 g. of distilled aluminum isopropylate. The mixture was refluxed for five hours, after which 250 cc. of isopropyl alcohol was distilled off over a period of four hours. The residue was poured into 1300 cc. of 3% potassium hydroxide solution and shaken vigorously. The product was extracted with ether, the solvent concentrated to 100 cc. and 100 cc. of acetone added. Crystals separated on cooling which, recrystallized from acetone, melted at 142°. The yield was 31 g.

Anal. Calcd. for $C_{27}H_{45}OCl$: C, 77.1; H, 10.7. Found: C, 77.0; H, 10.8.

Hydrogenation of 7-Hydroxycholesteryl Chloride.—To a solution of 1.2 g. of 7-hydroxycholesteryl chloride in 120 cc. of acetic acid was added 400 mg. of platinum oxide. The mixture was shaken for four hours with hydrogen at 45 pounds (3 atm.) pressure after which the solution was filtered and concentrated. The residue was crystallized from acetone. It melted at 115° and mixed with cholestyl chloride it gave no depression in melting point.

Anal. Calcd. for $C_{27}H_{47}Cl$: C, 79.6; H, 11.6. Found: C, 79.7; H, 11.7.

The mother liquors from the above experiment were evaporated to dryness, the residue was dissolved in 15 cc. of glacial acetic acid at 50° and 0.2 g. of chromic oxide in 2 cc. of acetic acid added. After maintaining the solution at 50° for four hours it was kept at room temperature for an additional fifteen hours. Water was then added, the product extracted with ether, the ether evaporated and the residue crystallized from alcohol. Mixed with 7-keto-cholestyl chloride previously prepared, there was no depression in its melting point of 137°. This showed that the mother liquors contained 7-hydroxycholestyl chloride.

Anal. Calcd. for $C_{27}H_{45}OCl$: C, 77.1; H, 10.7. Found: C, 77.1; H, 10.9.

Benzoate of 7-Hydroxycholesteryl Chloride.—A solution of 22.6 g. of 7-hydroxycholesteryl chloride in 150 cc. of dry pyridine was cooled in ice and 50 cc. of benzoyl chloride was added in small portions with shaking. The solution was allowed to stand at room temperature for two days after which it was poured into 4 liters of water and allowed to stand overnight. The water was decanted and the residue dissolved in ether, the ether solution being washed with sodium carbonate solution after which it was concentrated to 100 cc. and 200 cc. of methyl alcohol added. After standing overnight, crystals formed which were recrystallized from acetone. The yield was 11 g. and the melting point 119°.

Anal. Calcd. for $C_{34}H_{49}O_2Cl$: C, 77.9; H, 9.4. Found: C, 78.2; H, 9.6.

Summary

epi-Cholesterol was prepared from the hydrolysis of 7-keto-cholesteryl chloride with potassium acetate followed by reduction of the ketone group by the Wolff–Kishner method. Catalytic reduction by platinum oxide in acetic acid of either 7-keto-cholesteryl chloride or 7-hydroxycholesteryl chloride gave a mixture of cholestyl chloride and 7-hydroxycholestyl chloride. Derivatives of the various products were prepared.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Physical Studies of Non-aqueous Solvates. II. The Vapor Pressure of Magnesium Bromide–Diethyl Ether Solutions

BY H. H. ROWLEY[1]

The vapor pressure of an ethyl ether solution saturated with magnesium bromide was reported by Evans and Rowley[2] to be 410 mm. at +25°. Scherer and Newton,[3] using the vapor pressure values of magnesium bromide–ethyl ether systems to calculate the free energy of formation of magnesium bromide, also reported a value of 410 mm. at +25° for a solution of ether saturated with magnesium bromide. It is a well established fact[2,4] that magnesium bromide with excess ethyl ether forms two conjugate liquid phases at +25°, the upper layer consisting of ether saturated with magnesium bromide (3.23 g./100 g. Et_2O), the bottom layer containing about 39% magnesium bromide. Re-examination of the data of Evans and Rowley indicated that under the conditions of the experiment the only liquid present was the oily bottom layer containing about 39% magnesium bromide and absolutely none of the light upper layer. Thus, the vapor pressure reported was not for an ethyl ether solution saturated with magnesium bromide.

In order to prove this, the vapor pressure of the two conjugate liquid phases has now been measured over a temperature range from 0 to +25°. The system also has been studied in more detail at +25° varying the ratio of $MgBr_2:Et_2O$ from $^1/_4$ to 1.

Experimental

Apparatus.—The vapor pressures were measured by the static method as shown in Fig. 1. The samples were placed in a flat-bottomed flask (A), about 4 cm. in diameter and 5 cm. in height, sealed to a Pyrex spiral (B) about 4 cm. in diameter and 16 cm. in length, connected to a mercury U-manometer (C). The flexible glass spiral together with the relatively large surface of the sample, allowed the sample to be agitated vigorously by gently tapping the flask (A). Thus, thorough mixing and equilibrium conditions were attained rapidly. The mercury in the manometer (C) could be raised or lowered by adjusting the pressure in reservoir (D) and served also to seal the sample from the rest of the system and protect it from stopcock grease. When it was necessary to evacuate the space above the sample, the mercury was lowered and the sample

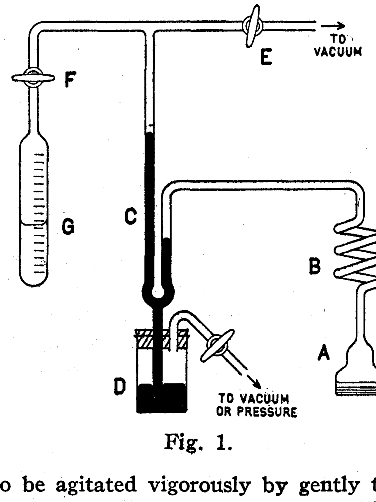

Fig. 1.

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[1] Department of Chemistry, State University of Iowa, Iowa City, Iowa.

[2] W. V. Evans and H. H. Rowley, THIS JOURNAL, **52**, 3523 (1930).

[3] Geo. A. Scherer and Roy F. Newton, *ibid.*, **56**, 18 (1934).

[4] (a) H. H. Rowley, *ibid.*, **58**, 1337 (1936); (b) B. N. Menschutkin, *Z. anorg. Chem.*, **49**, 34 (1906).

connected directly to a Cenco Hy-Vac pump (protected from ether vapor by activated charcoal at −78°) through stopcock (E). During the measurements, stopcock (E) was always connected to the vacuum pump so the vapor pressure values could be read directly on the manometer (C). All the connecting tubes were of 8-mm. Pyrex glass.

Dry, distilled ether was stored in tube (G) sealed to the system and cut off by stopcock (F). Thus, ether could easily be distilled from or added to the sample by lowering the mercury in (C) and immersing the ether tube (G) or the sample flask (A) in a mixture of carbon dioxide and acetone. The ether reservoir was calibrated in 0.5 cc. and the volume could be read to less than 0.2 cc.

This type of apparatus had the advantage of a relatively small volume above the sample, very little of it outside the bath and no stopcocks or joints in contact with the ether vapor whose pressure was being measured. The room temperature was always kept above +25° during the measurements to prevent any condensation of ether vapor when the sample was at +25°.

Procedure.—The magnesium bromide–ethyl ether solution was prepared in an Erlenmeyer flask, taking the usual precautions against moisture and light.[4a] The two-layer system was transferred to a dry sample flask, cooled to −78° in a carbon dioxide–acetone mixture and sealed to the apparatus. The apparatus was evacuated for about thirty minutes with the sample at −78°. The mercury was then raised in the U-manometer and the sample brought to +25° and agitated until it was completely liquid again. The first measurements made at +25° were invariably high due to occluded gases which were released on melting the sample. To remove these, the sample was again cooled to −78°, where the normal vapor pressure is about 0.6 mm. and the "occluded" gases, which did not condense, pumped off. Generally, one such treatment was sufficient to remove these gases and the vapor pressure of the system would give reproducible values at a constant temperature.

Ether was distilled from the sample at intervals and condensed in the reservoir (Fig. 1, G) and its volume measured at +25°. From this value and the density of ether at +25°, the grams and hence the moles of ether distilled could be calculated. When all the ether had been distilled from the sample and the experiment completed, the sample flask was filled with dry air, cut off and weighed. It was then cleaned and weighed again and the weight of anhydrous magnesium bromide determined. From these data, the mole ratio of magnesium bromide to ethyl ether could be calculated for any series of measurements. Some experiments also were made by desolvating the sample and weighing before sealing to the apparatus. Known amounts of ether were then distilled onto the sample and measurements made.

The flasks were kept at constant temperature by means of water-baths in vacuum flasks. At 0° the melting point of ice was used. The 0.1° thermometers were calibrated at 0° and at the transition point of sodium sulfate decahydrate. The temperature measurements were accurate to ±0.03°. The manometer readings were corrected to 0° by values obtained from the "International Critical Tables"[5] and were accurate to ±0.5 mm.

Results.—The values for the vapor pressures of ethyl ether solutions saturated with magnesium bromide between 0 and +25° are shown in Table I. In all cases there was excess ether present. The equilibrium phase at temperatures below 12° is solid magnesium bromide triethyl etherate, between 12 and 22.5° it is the solid diethyl etherate, and above 22.5° the immiscible liquid containing about 39% magnesium bromide.[4a] The vapor pressure for dry redistilled ethyl ether determined in the same apparatus is also included in Table I for comparison. The values for the vapor pressure lowering shown in column 4 were measured directly by connecting one side of the manometer to the ether reservoir at the same temperature as the sample. These readings were made with a Cenco Comparator accurate to ±0.1 mm.

TABLE I

VAPOR PRESSURE OF ETHYL ETHER SOLUTIONS SATURATED WITH MAGNESIUM BROMIDE

Temp., °C.	V. p. of Et_2O, mm.	V. p. of satd. soln., mm.	ΔP^a mm.
0	186.7 ± 0.1	185.7 ± 0.1	1.1
5	234 ± 0.5	233 ± 0.5	
10	292	290	
15	361	359	2.1
20	442	438	
25	537	532	5.1

[a] Values in col. 4 were measured directly on a differential manometer with an accuracy of ±0.1 mm.

A series of experiments also was run at 25° in which the ratio of ethyl ether to magnesium bromide was varied. Whenever sufficient ether was present to form two conjugate liquid phases, the value for the vapor pressure of the system was always 532 mm. at +25°. However, as the ether was removed from the sample at 25°, the light upper layer became smaller and finally disappeared. At this point, the vapor pressure of the system began to decrease as the ratio of ether to magnesium bromide was lowered, fairly rapidly if only one liquid phase was present but not so rapidly if two phases, liquid and crystal, appeared. As the mole ratio of magnesium bromide to ethyl ether approached 1:2.0, the values dropped off very rapidly until they were about 390 mm. when all the liquid phase had disappeared and only crystals remained. This value for the vapor pressure of magnesium bromide diethyl etherate in equilibrium with the monoethyl etherate remained constant from a mole ratio of 1:2.0 to 1:1.0. The results of a group of measurements are shown in Table II.

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(5) "International Critical Tables," Vol. I, 1928, pp. 68–69.

TABLE II

CHANGE OF VAPOR PRESSURE AT +25° WITH MOLE RATIO

Mole ratio $MgBr_2 : Et_2O$	Vapor press. immiscible layer, mm.	Vapor press. immiscible layer with crystals, mm.	Vapor press. crystals, mm.
1:3.69	529		
1:3.58	523.5		
1:3.48	518.5		
1:3.32	511.5		
1:3.16	501.5		
1:3.05	481.5		
1:2.85	449.5	499.5	
1:2.64		502.5	
1:2.64		498.5	
1:2.58	397.5	492.5	
1:2.48		483.5	
1:2.38		498.5	
1:2.36		494.5	
1:2.32		480.5	
1:2.24		489.5	
1:2.00+		404	
1:1.99			389
1:1.92			392
1:1.86			385.5
1:1.84			389.5
1:1.28			392

Effect of Moisture.—Inasmuch as the presence of moisture is known to affect the apparent solubility of magnesium bromide in ethyl ether,[4a] several experiments were performed to determine its effect on the vapor pressure of the solutions. The solutions were made in the usual manner and placed in the sample flask. Before sealing to the apparatus, measured amounts of distilled water were added to the samples. In every case, a white precipitate formed at first but redissolved on agitation. The "moist" samples gave the appearance of being perfectly normal.

The measurements were made in exactly the same manner as for a dry sample. The results are shown in Table III. The vapor pressure of a "moist" two-layer system containing excess ether was found to be 531.5 mm. at 25° as compared to 532 mm. for the dry samples. After the disappearance of the light upper layer, the vapor pressure of the system decreased with decreasing amounts of ether as was found with a normal sample. However, for corresponding mole ratios, the values for the "moist" sample were always below those for the normal samples, being 50 to 100 mm. lower when the mole ratio was between 1:3.0 and 1:2.0.

Effect of Age.—The effect of the age of the sample on the vapor pressure was measured on one sample that had been sealed in a glass tube for over three months at +25°. The upper ether layer was colorless but the heavy immiscible layer had become a dark brown. The vapor pressure of the two layer systems at +25° was 531.5 mm. compared to 532 mm. for a fresh sample. The heavy immiscible layer gave values about 20 to 25 mm. below those for a fresh sample of corresponding composition. Whether this was due to some change in the solution (mixture had darkened with age) or to possible presence of moisture could not be determined.

TABLE III

EFFECT OF MOISTURE ON VAPOR PRESSURE AT +25°

Mole ratio $MgBr_2$: Et_2O	Mole ratio $MgBr_2$: H_2O (estimated)	Vapor press. immiscible layer, mm.	Vapor press. immiscible layer with crystals, mm.	Vapor press., crystals, mm.
1:3.96	1:0.05	530.5		
1:3.83	1:0.05	528		
1:3.70	1:0.05	523		
1:3.48	1:0.05	510.5		
1:3.34	1:0.05	501		
1:3.21	1:0.05	483.5		
1:2.95	1:0.05	448	467.5	
1:2.69	1:0.05		448.5	
1:2.65	1:0.2		447	
1:2.55	1:0.05		421	
1:2.42	1:0.2		412	
1:2.36	1:0.2		402	
1:2.12	1:0.2		398	
1:2.06	1:0.2		388.5	
1:1.98	1:0.05			387.5
1:1.53	1:0.2			360.5
1:1.50	1:0.05			368.5
1:1.18	1:0.2			327.5

Discussion

The values for the vapor pressures of ethyl ether solutions saturated with magnesium bromide as shown in Table I are only a few millimeters below those for pure ether. The lowering at 0° is 1.1 mm.; at +15°, 2.1 mm.; and at +25°, 5.1 mm.; the solubility of magnesium bromide at these temperatures is, respectively, 0.70 g., 1.72 g., 3.23 g./100 g. ethyl ether.[4a] Assuming the applicability of Raoult's law to solutions of these concentrations, the molecular weight of dissolved magnesium bromide (mol. wt. 184.2) as calculated is 88 at 0°, 220 at +15° and 252 at +25°. This apparent increase in molecular weight with increasing concentration is in agreement with the results of Meisenheimer and Schlichenmaier,[6] who studied the boiling point rise of ethyl ether solutions of ethylmagnesium bromide and magnesium iodide. However, too much stress should not be

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(6) Jakob Meisenheimer and Walter Schlichenmaier, *Ber.*, **61B**, 720 (1928).

placed on this apparent increase in molecular weight since it is highly probable that Raoult's law is not valid for this type of solution. The fact that these compounds form known solid solvates with ethyl ether and two of them form two conjugate liquid phases at room temperature, indicates that the solutions would not be ideal.

It should be noted that the vapor pressure of pure diethyl ether at 0° as recorded in this work is 186.7 ± 0.1 mm. compared to 185.3 mm. as given in the "International Critical Tables."[7] This value was checked with many carefully purified samples and with several modifications of the apparatus. The values obtained between +10 and +25° agree within the experimental error with the literature values.

Since the vapor pressure of the ethyl ether–magnesium bromide system was always constant at +25° if the mole ratio of magnesium bromide to ether was greater than 1:4.00, it appears justified to call 532 mm. the vapor pressure of a solution of ethyl ether saturated with magnesium bromide. Reference to the solid line in Fig. 2 and to Table II shows that when the mole ratio falls below 1:3.8, the two-layer system disappears leaving only the heavy bottom layer. As the mole ratio is decreased, the vapor pressure of the system falls rapidly along the line ABC as long as only one liquid phase is present. However, the portion of the curve BC appears to be metastable, for if a crystal phase appears the vapor pressure rises to a value on the curve BD. Thus, between the mole ratios 1:3.3 and 1:2.0, the three phase system: magnesium bromide dietherate crystals—a concentrated solution of magnesium bromide in ethyl ether–ether vapor, is stable. As the ether is removed from the system, the liquid phase diminishes with a correspondingly slight decrease in vapor pressure except as the system approaches a mole ratio of one magnesium bromide to two ethyl ethers. At this point (E) the liquid phase disappears, leaving the crystals of magnesium bromide diethyl etherate. Further removal of ether does not change the vapor pressure of the system magnesium bromide dietherate–magnesium bromide monoetherate–ether vapor until the mole ratio has dropped to 1:1.

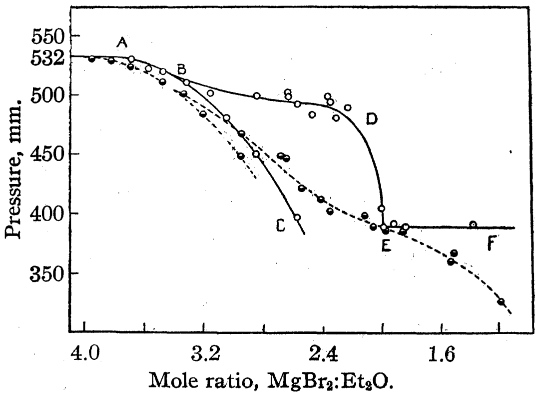

Fig. 2.—○, Dry sample; ◒, "Moist" sample.

The presence of moisture is shown to have a decided effect on the vapor pressure of the system as indicated in Table III and Fig. 2. Above a mole ratio of 1:4.0, the values for a "moist" sample are about 0.5 mm. below those for a normal sample. Below a mole ratio of 1:4.0 the vapor pressure of the liquid phase parallels that of a dry sample but is consistently below it as shown by the broken line in Fig. 2. The appearance of a crystal phase raises the values somewhat but they are considerably below those for a normal sample of the same composition. It is interesting to note that below a mole ratio of 1:2.0, the vapor pressure of the "moist" sample does not appear to remain constant. This might be due to slow equilibrium, though several of the values showed no increase after twenty-four hours.

The present work appears to show that the vapor pressure of an ethyl ether solution saturated with magnesium bromide is not 410 mm. at +25° as reported by Evans and Rowley[2] and Scherer and Newton[3] but is 532 mm. In the case of Evans and Rowley, it is definitely known that under the conditions of the experiment, the mole ratio of the system measured was below 1:3.0 and that there was the possibility of a trace of moisture being present. Reference to Fig. 2 shows that under these conditions it would be very possible to obtain a value such as was reported. It is likewise probable that Scherer and Newton[3] encountered the same difficulty.

Summary

1. The vapor pressure of diethyl ether saturated with magnesium bromide has been measured over the temperature range from 0 to +25°, and in more detail at 25° with variations in the ratio between magnesium bromide and ether from $^1/_4$ to 1.

2. The presence of small amounts of moisture

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[7] "International Critical Tables," Vol. III, 1928, p. 219.

was found to alter greatly the vapor pressure of the magnesium bromide–ethyl ether system. This fact was advanced as a possible explanation for the low values reported in the literature by several authors.

EVANSTON, ILL. RECEIVED JANUARY 2, 1937

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

The Effect of Iodine on the Rates of Decomposition of Formaldehyde, Acetaldehyde and Propionaldehyde

BY G. K. ROLLEFSON AND R. FRANCIS FAULL

In a previous note[1] we have presented data which show that the accelerating effect of iodine in a number of decompositions of simple organic molecules is due to a cycle of reactions involving destruction and re-formation of the iodine molecules. That work has been extended for the aldehydes so that now it is possible to give the mechanism in detail. These systems were found to be more complex than was indicated previously in that the rate of disappearance of aldehyde was definitely greater than the rate of reaction between the corresponding alkyl iodide and hydrogen iodide as calculated from Ogg's data[2] on those reactions. In fact as the temperature was lowered from the range discussed before this discrepancy increased until with acetaldehyde (to take an extreme case) the observed rate was several times as large as the one calculated on our earlier assumptions. In this paper we shall show that this discrepancy may be accounted for if we take into consideration the free radicals and iodine atoms which are present under the experimental conditions.

The reaction vessel was of Pyrex, cylindrical in shape, 15 cm. long with plane windows at both ends; the volume was approximately 250 cc. The vessel was mounted in an electric furnace that was fitted with windows so as to allow a beam of light to be directed lengthwise through the reaction vessel. The temperature was measured by a chromel–alumel thermocouple that was placed in a well extending into the reaction vessel in such a manner as not to lie in the optical path through the vessel. The furnace could be kept constant within a degree by manually regulated rheostats. The pressure was measured by a click gage, used as a null instrument, and a system that consisted of a mercury manometer and a sulfuric acid manometer connected so the mercury manometer could be used for high pressures and the sulfuric acid manometer for low pressures. The reaction vessel was connected to a vacuum line and to an iodine storage bulb, each through a heated glass valve. The iodine storage bulb was immersed in a small oil-bath that could be heated to distil iodine into the reaction vessel. The connecting tubing to the click gage and glass valves was capillary, wound with resistance wire and electrically heated to prevent the condensation of iodine. The dead space in the connections was about 2 cc.

The concentration of iodine during the course of a reaction was determined by measuring the intensity of a beam of light which passed through the reaction vessel. The light source was a thirty-two candle power automobile lamp connected through a resistance to a storage battery. A Corning glass filter No. 428 was placed between the lamp and the furnace window. The light transmitted by this filter is in the region of the maximum absorption by iodine. It has been pointed out by Cuthbertson and Kistiakowsky[3] that good results may be obtained in measuring the absorption of iodine with a blue filter while without the filter the effect of foreign gases on the absorption of iodine would cause a large error. The intensity of the beam was measured by a Weston Photronic Cell, No. 594, connected to a D'Arsonval galvanometer.

The acetaldehyde and propionaldehyde were taken from the center fractions of carefully dried Eastman Kodak Co. stock. Each sample was distilled several times and stored in three-liter bulbs connected to the vacuum line. No trouble from polymerization was experienced in storing the gases. The formaldehyde was prepared by heating trioxymethylene in a 500-cc. flask in an oil-bath. Above 200° the amount of polymer that exists in gaseous formaldehyde is very small; so no polymer could have existed in our experiments at 500°. The methyl iodide was prepared and stored similarly to the acetaldehyde. The iodine was a Merck reagent.

In order to determine the concentration of iodine present during the course of an experiment, it was necessary to make a calibration of the intensity measuring system. This was done by introducing certain amounts of iodine into the reaction vessel and by taking both the pressure reading and the galvanometer deflection. A curve could be constructed giving the relation of the light absorbed to the pressure of the iodine. To compensate for the small changes in light intensity and absorption in the reaction vessel due to tarring the galvanometer deflection with no iodine in the system was adjusted by varying the current passing through the light source.

The general procedure during a particular experiment was to introduce a certain desired amount of iodine vapor and read the pressure with the sulfuric acid manometer. The aldehyde, under higher pressure, was then introduced rapidly and an electric clock started simultaneously.

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[1] Faull and Rollefson, THIS JOURNAL, **58**, 1755 (1936).

[2] Ogg, *ibid.*, **56**, 526 (1934).

[3] Cuthbertson and Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).

Pressure readings could be obtained conveniently with the mercury manometer at one-half or one minute intervals. In order to find the initial pressure of aldehyde a graphical extrapolation to zero time was made. This value was corrected for the iodine present and also for the initial rapid increase due to the formation of three molecules from one of aldehyde and one of iodine. This latter correction was necessary because in every case the iodine had disappeared almost completely before the first pressure reading could be made.

In regard to the measurements on the iodine during the steady state it was observed that the concentrations were very low. In no case was the concentration over 5% of the initial iodine. The tarring that inevitably accompanies a reaction of this type made an exact determination impossible. To avoid these uncertainties we assumed in our calculations that the concentrations of hydrogen iodide and alkyl iodide were equal to the iodine added during the steady state. No great error could have been introduced by this assumption. When the reactions were complete the observed end-point was never quite equal to the theoretical end-point. This discrepancy was caused by a simultaneous condensation reaction and amounted to about 10 or 15% in the pressure reading. The magnitude of the difference was distributed quite randomly through the different runs. As nothing is known about this side reaction no correction was made in the calculation.

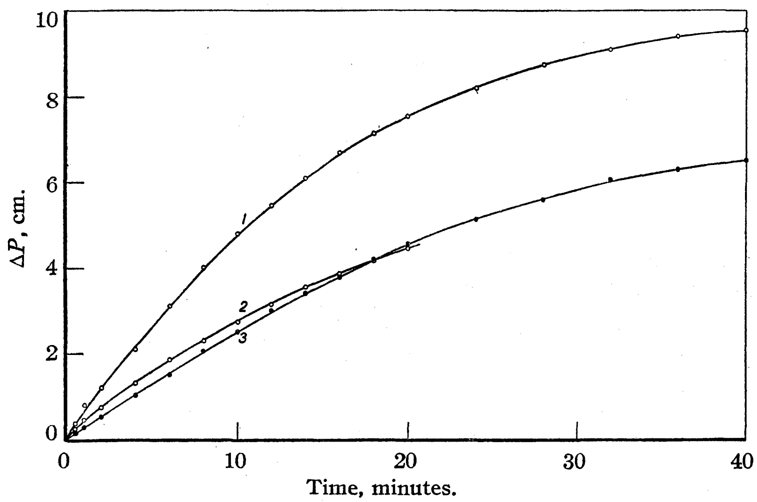

Fig. 1.—Curves 1 and 2 show the pressure increase in reactions with the initial pressure of formaldehyde 14.00 cm. and 11.20 cm., respectively. Curve 3 shows the pressure increase in a reaction mixture containing 11.38 cm. of formaldehyde and 1.06 cm. of iodine. The temperature was 500° in all experiments.

Results and Discussion

Formaldehyde.—Formaldehyde is known to decompose into hydrogen and carbon monoxide at temperatures in the neighborhood of 500° and above at an appreciable rate.[4] On introducing iodine to the thermal reaction mixture at 500° there is no noticeable increase in the rate of decomposition as shown by the curves in Fig. 1 although the iodine color disappears rapidly. Assuming that iodine reacts with formaldehyde according to the equation

$$\mathrm{HCHO} + \mathrm{I_2} = 2\mathrm{HI} + \mathrm{CO}$$

the limiting rate of any cycle of reactions is the rate of regeneration of iodine by the bimolecular decomposition of hydrogen iodide. This rate may be calculated from the work of Bodenstein as summarized by Kassel[5] the equation being

$$\mathrm{d(I_2)/d}t = 5.65 \times 10^{12} T^{1/2} e^{-46,116/RT}\ \mathrm{(HI)^2\ cc./mole/sec.}$$

At 500°, expressing the concentrations in cm. and the time in minutes, this equation reduces to

$$\mathrm{d(I_2)/d}t = 1.74 \times 10^{-3}\ \mathrm{(HI)^2}$$

On the introduction of 1 cm. of iodine the pressure of hydrogen iodide would become 2 cm., and the time required to produce a 1-cm. change is two hours and twenty-four minutes. This rate is only about one-fiftieth as fast as the thermal decomposition of formaldehyde, so no appreciable catalytic effect of iodine should be observed. Also, since there is no observed effect other than the disappearance of iodine, we may conclude that there is no reaction between formaldehyde and hydrogen iodide that is comparable to the thermal decomposition.

Acetaldehyde and Propionaldehyde.—The decompositions of acetaldehyde and propionaldehyde into methane and carbon monoxide and ethane and carbon monoxide, respectively, at temperatures above 350° are markedly accelerated by the addition of a small amount of iodine. Above 400° these systems change rapidly to a condition in which the concentration of free iodine is so low that it cannot be detected by absorption measurements. In this state the net reaction is the decomposition of the aldehyde. As the aldehyde concentration is decreased a point is reached at which the iodine color begins to reappear and as the aldehyde concentration decreases the free iodine concentration increases until when the aldehyde is completely decomposed all the original iodine is in the free state. At

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(4) Fletcher, *Proc. Roy. Soc.* (London), **A146**, 357 (1934).

(5) Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., New York, 1932, p. 150.

lower temperatures the free iodine is not removed so completely although at 350° it is still less than 5% of the amount originally added. Furthermore our measurements show that this low concentration is constant (within 10%) so that we may consider that we are dealing with a steady state in which the net result is a catalysis. If we assume that the catalysis is due to the reactions

$$RCHO + I_2 = RI + HI + CO$$
$$RI + HI = I_2 + RH$$

then the rate determining step will be the one between the alkyl iodide and hydrogen iodide. The rates of reaction between methyl iodide and hydrogen iodide and ethyl iodide and hydrogen iodide have been studied by Ogg over a temperature range from 250 to 320°.[2] If we extrapolate his rate equations to temperatures of the systems under consideration we find the results tabulated in Tables I and II. The first table shows the data for a typical experiment with acetaldehyde. The third column gives the observed rate and the fourth the rate calculated assuming that every molecule of iodine has reacted to give one of methyl iodide and one of hydrogen iodide. The difference tabulated in the last column shows a marked trend with the aldehyde pressure. Similar results were obtained with propionaldehyde as shown in Table II, although in this case the discrepancy between the observed and calculated rates is less at all pressures than with acetaldehyde. At low aldehyde pressures the system goes out of the steady state and the calculated rates are no longer valid; so the discrepancy cannot be followed to its limiting value.

TABLE I

ACETALDEHYDE WITH 0.41 CM. OF IODINE AT 364°

Time, min.	Press. ald., cm.	Obsd. rate, cm./min.	Calcd. rate, cm./min.	Diff., cm./min.
2	17.02	1.31	0.20	1.11
4	14.67	1.01	.20	0.81
6	13.02	0.79	.20	.59
8	11.52	.68	.20	.48
10	10.57	.59	.20	.39
12	9.17	.49	.20	.29
14	8.27	.41	.20	.21

TABLE II

PROPIONALDEHYDE WITH 0.42 CM. OF IODINE AT 350°

Time, min.	Press. ald., cm.	Obsd. rate, cm./min.	Calcd. rate, cm./min.	Diff., cm./min.
2	12.64	1.10	0.44	0.66
4	10.69	0.90	.44	.46
6	9.09	.77	.44	.33
8	7.49	.68	.44	.24
10	6.29	.57	.44	.13
12	5.09	.44	.44	.00

In seeking an explanation for this high rate of reaction we turned to a consideration of the mechanism given by Ogg for the reactions between the alkyl iodides and hydrogen iodide. His rate laws are of the form

$$\frac{-d(RI)}{dt} = k_1\,(RI)\,(HI) + k_2\,\frac{(RI)(HI)}{(HI) + (I_2)}$$

In this equation the first term is attributed to a simple bimolecular reaction and the second term is due to a series of reactions involving dissociation of the alkyl iodide into an iodine atom and an alkyl radical as the primary step. Now it has been shown by Leermakers,[6] Allen and Sickman[7] and Fletcher and Rollefson[8] that the decomposition of acetaldehyde is catalyzed at these temperatures by free radicals. Therefore if Ogg's mechanism is correct the high rate of reaction of the aldehyde might be accounted for as due to the catalysis by the free radicals produced in the thermal dissociation of the methyl iodide. In order to test this hypothesis several experiments were performed in which a small amount of methyl iodide was added to the acetaldehyde. Some reaction occurred but it was only about one-tenth as fast as with a corresponding amount of iodine. The observed rates in these experiments were found to be proportional to the square root of the pressure of the methyl iodide as it should be if the free radical mechanism were correct. Similar tests with hydrogen iodide showed no marked effect. This result shows that it is necessary to assume that either there is some source of free radicals other than the decomposition of methyl iodide or the iodine atoms present have a marked catalytic action for the decomposition of the aldehyde. We have tested a number of possibilities but the following set of reactions is the most completely in accord with the experimental facts, while the system is in the steady state.

$$I_2 \rightleftarrows 2I \qquad (1)$$
$$RI \rightleftarrows R + I \qquad (2)$$
$$R + RCHO \longrightarrow R + RH + CO \qquad (3)$$
$$I + RCHO \longrightarrow R + HI + CO \qquad (4)$$
$$R + HI \longrightarrow RH + I \qquad (5)$$
$$R + I_2 \longrightarrow RI + I \qquad (6)$$

In this set of reactions it is to be noted that the sum of (4) and (5) is essentially the decomposi-

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(6) Leermakers, THIS JOURNAL, **56**, 1537 (1934).

(7) Allen and Sickman, *ibid.*, **56**, 2031 (1934).

(8) Fletcher and Rollefson, *ibid.*, **58**, 2135 (1936).

tion of the aldehyde catalyzed by iodine atoms. Also according to Ogg the specific reaction rates of (5) and (6) are equal and since in our experiments the concentration of hydrogen iodide was always at least twenty times that of iodine, (6) is of minor importance and is included only for the sake of completeness. If we apply the usual methods of equating the rates of formation and removal of the intermediates R and I we find that the above set of reactions leads to the equation

$$k_1(\mathrm{I_2}) + 2k_2(\mathrm{RI}) = 2k_2'(\mathrm{R})(\mathrm{I}) + k_1'(\mathrm{I})^2$$

in which k_1' and k_2' represent the specific reaction rates for the reverse of (1) and (2), respectively, and k_1 and k_2 refer to the direct reactions. From an inspection of the reactions listed it may be seen that the net over-all reaction is the decomposition of the aldehyde. Under such conditions the equilibria in reactions (1) and (2) will not be disturbed, therefore we may write

$$\begin{aligned} k_1(\mathrm{I_2}) &= k_1'(\mathrm{I})^2 \\ k_2(\mathrm{RI}) &= k_2'(\mathrm{R})(\mathrm{I}) \end{aligned}$$

and

$$\begin{aligned} (\mathrm{I}) &= \sqrt{K_1(\mathrm{I_2})} \\ (\mathrm{R}) = K_2\frac{(\mathrm{RI})}{(\mathrm{I})} &= K_2(\mathrm{RI})/\sqrt{K_1(\mathrm{I_2})} \end{aligned}$$

in which K_1 and K_2 are the equilibrium constants for (1) and (2), respectively. Calculating the rate of disappearance of aldehyde by these reactions we have

$$\begin{aligned} -\frac{\mathrm{d(RCHO)}}{\mathrm{d}t} &= k_3\frac{K_2(\mathrm{RI})(\mathrm{RCHO})}{\sqrt{K_1(\mathrm{I_2})}} + k_4(\mathrm{RCHO})\sqrt{K_1(\mathrm{I_2})} \\ &= (\mathrm{RCHO})\left[\frac{k_3K_2(\mathrm{RI}) + k_4K_1(\mathrm{I_2})}{\sqrt{K_1(\mathrm{I_2})}}\right] \end{aligned}$$

In any given experiment when the system has reached the steady state (RI) and $(\mathrm{I_2})$ are constant and proportional to the initial amount of iodine. Let $(\mathrm{I_2})_0$ equal the pressure of iodine added and α be the fraction remaining as $\mathrm{I_2}$ with $1-\alpha$ the fraction as RI and HI. Then our equation becomes

$$-\frac{\mathrm{d(RCHO)}}{\mathrm{d}t} = (\mathrm{RCHO})(\mathrm{I_2})_0{}^{1/2}\left[\frac{k_3K_2(1-\alpha)}{K_1{}^{1/2}\alpha^{1/2}} + k_4K_1{}^{1/2}\alpha^{1/2}\right]$$

All the quantities contained within the brackets are constants when the system is in the steady state so the rate of removal of aldehyde is proportional to the aldehyde pressure and the square root of the initial iodine pressure. The only one of these quantities which could be considered as having a possibility of varying in the steady state is α. The absolute value of α will depend upon the relative rates of formation and disappearance of the iodine. The rate of formation depends upon the concentrations of the alkyl iodide and hydrogen iodide according to the law given by Ogg

$$\frac{\mathrm{d(I_2)}}{\mathrm{d}t} = k_1(\mathrm{RI})(\mathrm{HI}) + k_2\frac{(\mathrm{RI})(\mathrm{HI})}{(\mathrm{HI}) + (\mathrm{I_2})}$$

In what we have called the steady state (RI) = (HI) and both are constant and approximately equal to the iodine added. The rate expression just given therefore reduces to ($(\mathrm{I_2})_0$ is the iodine originally added)

$$\mathrm{d(I_2)d}t = k_1(\mathrm{I_2})_0^2 + k_2(\mathrm{I_2})_0$$

and since under the conditions of our experiment the second term is much larger than the first we may say that the rate of formation of iodine is approximately proportional to the amount originally added. In the steady state the rate of disappearance of iodine, whatever law it follows, is the same as its rate of formation. Under these conditions the only reactant which is changing appreciably is the aldehyde, therefore if the rate is to depend on α and the aldehyde pressure it must do so in such a way that the effect of any change in the aldehyde pressure is offset by a corresponding change opposite in sign in α. Our measurements in the steady state are sufficiently accurate to show that this is definitely not the case but that α is independent of the aldehyde as long as the steady state conditions exist. Since there is no other variable we must conclude the α is constant.[9] The breakdown of the steady state at pressures of 5–6 cm. of acetaldehyde or 3–5 cm. of propionaldehyde corresponds to the deviation of α from constancy.

The rate equation just derived does not give the total rate of disappearance of aldehyde but only that part due to the presence of free radicals and iodine atoms. There still remains a certain amount of decomposition according to the mechanism

$$\begin{aligned} \mathrm{I_2} + \mathrm{RCHO} &\longrightarrow \mathrm{RI} + \mathrm{HI} + \mathrm{CO} \\ \mathrm{RI} + \mathrm{HI} &\longrightarrow \mathrm{RH} + \mathrm{I_2} \end{aligned}$$

These reactions contribute a term $k(\mathrm{RI})(\mathrm{HI})$ which is identical with the first term of the rate law given by Ogg for the reaction between the alkyl iodide and hydrogen iodide. The second term of Ogg's law corresponds to reactions which have already been taken into account in the

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(9) A law for the disappearance of iodine which would fit these conditions is $-\mathrm{d(I_2)}/\mathrm{d}t = k\alpha(\mathrm{I_2})_0(\mathrm{RCHO})/1 + k'(\mathrm{RCHO})$ but we have no direct evidence for such a law nor is it obvious how such a law could be obtained.

mechanism involving free radicals. The total rate of disappearance of aldehyde may be written

$$-\mathrm{d}(\mathrm{RCHO})/\mathrm{d}t = k(\mathrm{RI})(\mathrm{HI}) + k'(\mathrm{RCHO})(\mathrm{I_2})_0^{1/2}$$

where the first term may be calculated from Ogg's data and the second term is that due to the free radical mechanism already discussed with all the constants grouped together in k'. In order to test this expression we have determined the rates of reaction in the region where the iodine is principally in the form of alkyl iodide and hydrogen iodide. The observed rates for a typical experiment are given in column three, Table III. The next column gives the difference between this rate and the k(RI)(HI) as calculated from Ogg's equation. The last column gives the values of k' assuming our rate law to hold. In Tables IV and V the results are given for acetaldehyde and propionaldehyde, respectively, in a number of experiments with different amounts of iodine added. From the constancy of the value of k' the results may be said to be in agreement with the rate law as given above.

TABLE III

ACETALDEHYDE WITH 1.38 CM. OF IODINE AT 364°

The value of k(RI)(HI) is 0.24 cm./min.

Time, min.	Press. ald., cm.	Obsd. rate, cm./min.	$k'(\mathrm{RCHO})(\mathrm{I_2})_0^{1/2}$	k'
2	14.41	1.57	1.33	0.0785
4	11.81	1.30	1.06	.0764
6	9.31	1.11	0.87	.0795
8	7.21	0.90	.66	.0779
10	5.71	.65	.41	.0610

TABLE IV

ACETALDEHYDE AT 364°

Press. I_2, cm.	Range of ald. press., cm.	k(RI)(HI)	Average $k'(\mathrm{I_2})_0^{1/2}$	Average k'
0.41	17.02–8.27	0.021	0.056	0.086
.52	16.59–5.69	.034	.070	.097
.71	15.40–5.95	.063	.082	.098
.95	14.55–6.65	.113	.086	.088
1.38	14.41–5.71	.238	.092	.078

TABLE V

PROPIONALDEHYDE AT 350°

Press., I_2, cm.	Range of ald. press., cm.	k(RI)(HI)	Average $k'(\mathrm{I_2})_0^{1/2}$	Average k'
0.42	12.64–5.09	0.055	0.081	0.125
.60	13.35–7.40	.112	.087	.112
.77	11.67–4.27	.187	.105	.119
.80	7.85–3.00	.199	.105	.117
.81	10.18–4.33	.202	.112	.125
1.21	7.37–3.42	.455	.144	.131

The equation we have been discussing is strictly valid only when the system is in what may be called a steady state with respect to iodine, *i. e.*, the amount of free iodine present is essentially constant. This condition is fulfilled when the ratio of aldehyde to iodine added is large. Toward the end of an experiment when this ratio is becoming small the values of k' decrease due to the increase in α. Experimentally it was found that the decrease in k' coincided with the return of the iodine color.

On the basis of our mechanism the apparent order of the reaction with respect to aldehyde will depend on the relative importance of the two terms in the rate law. Thus with acetaldehyde the second term accounts for the major portion of the rate and therefore the reaction appears to be of approximately first order with respect to acetaldehyde. With propionaldehyde the first term is more important and therefore the apparent order with respect to propionaldehyde is somewhat less than the first order.

Summary

The addition of iodine markedly accelerates the decompositions of acetaldehyde and propionaldehyde but does not affect the decomposition of formaldehyde appreciably. It is shown that these effects can be explained by assuming that the iodine reacts with the aldehyde first and this step is followed by two parallel sets of reactions. The first is a simple bimolecular reaction of the alkyl iodide and hydrogen iodide formed from the above-mentioned reaction. The second is a series of reactions involving the free radicals and iodine atoms produced by the thermal dissociations of the alkyl iodide and the residual iodine. Detailed mechanisms are presented and it is shown that they fit the experimental facts.

BERKELEY, CALIF. RECEIVED DECEMBER 22, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 581]

The Formula of Ammonium Paramolybdate

BY J. H. STURDIVANT

In 1917 Rosenheim[1] advocated for the paramolybdates the formula $R_5H_5[H_2(MoO_4)_6]$. The previously accepted formula had described the compounds as heptamolybdates, $R_6Mo_7O_{24}\cdot 4H_2O$. Analytical methods were unable to decide between the two formulas until recently, when the heptamolybdate formula was reaffirmed on the basis of analyses of mixed paramolybdates of ammonia and triethanolamine.[2]

In the present paper additional evidence for the heptamolybdate formula will be described, based on X-ray measurement of the lattice constants and a determination of the density of crystalline ammonium paramolybdate.[3]

Cooling a saturated ammoniacal solution of Powers–Weightman–Rosengarten ammonium molybdate, C. P. grade, produced crystals in the form of rhomboidal plates about 2 mm. × 1 mm. × 1/3 mm. Forms observed, in the notation of Groth,[4] were $b(010)$, $o(111)_G$, $n(310)_G$, $m(110)_G$. As foreshadowed by the habit of the crystals, the X-ray investigation required a new assignment of axes, which will be used throughout this paper. The new axis **a** is taken parallel to $[10\bar{1}]_G$ of Groth, and the new axis **c** parallel to $\mathbf{c}_G$ of Groth. From the monoclinic angle 91°12′ given by Groth and the axial ratios of Groth, the value $\beta = 115°59'$ is calculated. From direct goniometric measurements on the plates used in this investigation, β was found to be $116°0' \pm 4'$. Monochromatic X-ray photographs were prepared by oscillating a crystal through small angles on each side of the primary beam to give selected orders of reflection from the *a*, *b* and *c* planes. The cylindrical camera of 5 cm. nominal radius was calibrated by the use of calcite as a standard crystal with the grating space given by Siegbahn.[5] Film shrinkage was allowed for by marks imposed on the film before development. The radiation was from a copper target. The following spacings[6] were obtained at about 24°:

$d_{(100)}$ = 7.534 ± 0.010 Å. from measurements of (100), (200), (300).
$d_{(010)}$ = 36.125 ± 0.008 Å. from measurement of (0·36·0).
$d_{(001)}$ = 9.405 ± 0.005 Å. from measurement of (0·0·10).

Layer line measurements and data from a Laue photograph proved that the corresponding axes describe a true unit of structure of minimum volume, and the unit was further shown by Laue data to be simple. Groth describes ammonium paramolybdate as monoclinic prismatic. Two Laue photographs taken with the X-ray beam approximately parallel to **a** indicated that interferences (*h*0*l*) with *l* odd do not occur. On oscillation photographs interferences (0*n*0) with *n* odd were absent. The space-group is therefore $C_{2h}^5 - P2_1/c$.

The density was measured of a 7-g. sample of the original commercial product, ground to pass through a 150-mesh sieve, and weighed in a pycnometer filled with carbon tetrachloride. During addition of the carbon tetrachloride the air was exhausted from the pycnometer and powder. The density was found to be 2.871 ± 0.003 at 25°.

The weight of a mole of unit cells is $0.6064 \times 10^{24} \times \rho \times d_{(100)} \times d_{(010)} \times d_{(001)} \times (\sin\beta)^{-1} = 4958 \pm 20$. The formula $(NH_4)_5H_5[H_2(MoO_4)_6]$ corresponds to a molecular weight of 1057; this number is contained 4.7 times in 4958; and 4.7 differs from an integer by more than the experimental error. On the other hand, four molecules of the heptamolybdate formula in the unit cell would give a weight equal to 1236.3 × 4 = 4945. The conclusion is therefore reached that the formula of ammonium paramolybdate is $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

The author is indebted to Professor Linus Paul-

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(1) A. Rosenheim, M. Pieck and J. Pinsker, *Z. anorg. allgem. Chem.*, **96**, 139–181 (1916).

(2) F. Garelli and A. Tettamanzi, *C. A.*, **29**, 7846[6] (1935); **30**, 4114[4] (1936).

(3) Molecular weight determinations by the methods of X-ray crystallography have been reported previously by D. Crowfoot, *Chemistry and Industry*, **54**, 568 (1935), and by D. Crowfoot and H. Jensen, THIS JOURNAL, **58**, 2018 (1936).

(4) P. Groth, "Chemische Kristallographie," W. Engelmann, Leipzig, 1908, Teil II, p. 603.

(5) M. Siegbahn, "Spektroskopie d. Röntgenstrahlen," Verlag von J. Springer, Berlin, 1931, pp. 44–45.

(6) The fundamental translations calculated from these spacings and $\beta = 116°0'$ are a = 8.382 Å., $b = d_{(010)}$, c = 10.464 Å. Thence the axial ratios $a_G:b_G:c_G$ = 0.6258:1:0.2897 are calculated. Groth gives, however, $a_G:b_G:c_G$ = 0.6297:1:0.2936. The disagreement is not surprising in view of the generally poor quality of the faces of ammonium molybdate crystals, which is reflected, for example, in the detailed measurements reported by P. Rossoni, *Atti soc. toscana sci. nat., proc. verb.*, **42**, 10–19 (1933). The nature of the imperfections, particularly the development of vicinal faces in the zone of [001], is, however, not such as to diminish seriously the accuracy of direct measurement of *β*.

ing for suggesting the study of ammonium paramolybdate.

Summary

The lattice constants, space groups and density of crystalline ammonium paramolybdate were determined. From the weight of the unit of structure it is concluded that the compound is a heptamolybdate, with the formula $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

PASADENA, CALIF. RECEIVED JANUARY 27, 1937

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

The Solubilities of Barium and Strontium Carbonates in Aqueous Solutions of Some Alkali Chlorides

BY R. W. TOWNLEY AND W. B. WHITNEY WITH W. A. FELSING

Object of the Investigation

A number of investigations dealing with the change in solubilities of the alkaline earth carbonates in aqueous salt solutions have been recorded. In each case an increase in solubility was noted. Muir[1] studied the solubility of calcium carbonate in sodium chloride solutions. Cameron and Robinson,[2] Cantoni and Goguelia,[3] and Dubrisay and François[4] studied the influence of potassium chloride upon the solubility of calcium carbonate and the last-named investigators also studied the influence of potassium chloride upon the barium carbonate solubility. De Coninck and Arzalier[5] briefly mention their study of the solubility of strontium carbonate in the presence of potassium chloride. In no case, however, was the study made with the view of determining the activity of these alkaline earth carbonates by the method outlined by Lewis and Randall.[6]

The purpose of this investigation, hence, was the determination of the influence of increasing concentrations of lithium, sodium, and potassium chlorides upon the solubilities of the normal carbonates of barium and strontium. It was hoped that the data obtained would yield information of value regarding the activities of these carbonates.

Previous Investigations

The solubility of barium carbonate in pure water has been reported[7] at various temperatures; McCoy and Smith's value at 25°, as calculated from their solubility product, is 0.90×10^{-4} g. moles/1000 g. of water. The solubility of strontium carbonate is also recorded by several investigators.[8] McCoy and Smith's value at 25° is 0.396×10^{-4} g. moles/1000 g. water.

Experimental Methods

The method of this investigation consisted of saturating solutions of lithium, sodium, and potassium chlorides at different concentrations (approx. 0.02, 0.06, 0.10, 0.2, 0.3, 0.5, 1.0, and 3.0 *M*) with the solid barium and strontium carbonates at both 25 and 40°. The finely divided solids, in large excess, were agitated with the various solutions in a shaking device immersed in a thermostat maintained at 25 ± 0.02° and at 40 ± 0.04°. After an interval of twenty-four to forty-eight hours of agitation (some samples were shaken for much longer periods without yielding different results, however), the flasks were allowed to stand for several hours in the thermostat; filtered samples were withdrawn at the thermostat temperature and were immediately titrated against hydrochloric acid, using phenolphthalein as indicator; each sample was heated to the boiling point as the end-point was approached. Weight burets were used throughout. Duplicate equilibrium determinations were made for each concentration and each determination was made in duplicate.

Water.—The best grade of conductivity water was used throughout, the final distillation being made from and into quartz. All water and solutions were protected against carbon dioxide.

The Carbonates.—(a) The barium carbonate was prepared from Merck C. P. precipitated barium carbonate. The carbonate was converted into the bicarbonate to form a very dilute solution; it was then re-precipitated by boiling, collected on a filter, washed with conductivity water, and dried for twelve hours at 250°. (b) The strontium carbonate was prepared from C. P. strontium chloride by the addition, in hot dilute solution, of the required amount of ammonium carbonate of reagent grade. The carbonate was repeatedly washed, filtered and dried for twelve hours at 250°.

The Chlorides.—(a) The lithium chloride was obtained by recrystallizing E. & A. "Pure" lithium chloride. The

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(1) Muir, *J. Chem. Soc.*, **37**, 60 (1880).

(2) Cameron and Robinson, *J. Phys. Chem.*, **11**, 577 (1907).

(3) Cantoni and Goguelia, *Bull. soc. chim.*, [3] **33**, 13 (1905).

(4) Dubrisay and François, *Compt. rend.*, **192**, 741 (1931).

(5) De Coninck and Arzalier, *Bull. acad. roy. Belg.*, 577 (1908).

(6) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, Chapter XXVIII.

(7) (a) Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 241 (1893); (b) McCoy and Smith, THIS JOURNAL, **33**, 468 (1911); (c) Seidell, "Solubilities," D. Van Nostrand Co., New York, 1919, p. 107.

(8) (a) Holleman, *Z. physik. Chem.*, **12**, 135 (1893); (b) Kohlrausch and Rose, *ibid.*, **12**, 241 (1893); (c) ref. 7b, p. 473.

solution was concentrated by slow evaporation in a vacuum desiccator containing concd. sulfuric acid. The filtered crystals were dried for ten hours at 250°. (b) The sodium chloride was prepared from Baker reagent grade by precipitation from solution by means of hydrogen chloride; the product was dried and then heated to the "crackling" point in a platinum dish. (c) The potassium chloride was recrystallized twice from conductivity water, washed, and dried for ten hours at 250°.

Hydrochloric Acid.—Constant boiling acid was used in preparing the 0.01 *M* acid for the titration of the equilibrium filtrates.

The Salt Solutions.—The chloride solutions were prepared by adding weighed quantities of water to carefully weighed quantities of the dried salts.

Experimental Data

The experimentally determined solubilities, both at 25 and 40°, were plotted to large scale against the molalities of the added chlorides. A "best" line was drawn through each set of data points; the data of Tables I and II at rounded concentrations were read off this best line.

Table I

Solubility of Barium Carbonate

Molality of added salt	"*C*," g. moles/1000 g. water (× 10^4) at 25° in			"*C*," g. moles/1000 g. water (× 10^4) at 40° in		
	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.00	0.9114	0.9114	0.9114	1.2217	1.2217	1.2217
.02	1.345	1.170	1.083	1.670	1.705	1.670
.05	1.970	1.515	1.330	2.175	2.220	2.075
.10	2.895	2.030	1.700	2.875	2.810	2.500
.20	4.325	2.875	2.260	4.060	3.680	3.025
.30	5.390	3.570	2.685	5.090	4.295	3.355
.40	6.260	4.180	3.005	6.075	4.655	3.590
.50	6.980	4.735	3.285	7.015	5.130	3.760
1.00	10.05	6.900	4.160	11.505	6.210	4.190
3.00	24.84	9.950	4.685	29.795	8.615	4.950

Table II

Solubility of Strontium Carbonate

Molality of added salt	"*C*," g. moles/1000 g. water (× 10^4) at 25° in			"*C*," g. moles/1000 g. water (× 10^4) at 40° in		
	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.00	0.5525	0.5525	0.5525	0.7026	0.7026	0.7026
.02	.957	.737	.672	1.164	.888	.975
.05	1.203	.965	.835	1.494	1.140	1.190
.10	1.455	1.320	1.055	1.845	1.505	1.415
.20	1.750	1.965	1.375	2.260	2.195	1.690
.30	1.925	2.485	1.570	2.525	2.780	1.870
.40	2.040	2.915	1.685	2.717	3.280	1.980
.50	2.135	3.285	1.756	2.870	3.710	2.055
1.00	2.440	4.415	1.900	3.390	5.145	2.205
3.00	3.405	6.855	2.176	5.060	8.665	2.480

Discussion and Treatment of Results

The solubilities of barium carbonate at 25 and 40° in pure water, as determined during this investigation, were 0.9114 and 1.2217 × 10^{-4} g. moles/1000 g. of water, respectively. The value at 25° agrees well with the value of McCoy and Smith,[7b] indicating that the method of analysis of this investigation yielded satisfactory results. The solubilities of strontium carbonate at 25 and 40° in pure water were found to be 0.5525 and 0.7026 × 10^{-4} g. moles/1000 g. of water, respectively. The value at 25° lies between that of Kohlrausch and Rose[8b] at 24° and that of McCoy and Smith[8c] at 25°. The average heats of solution for barium carbonate and strontium carbonate into their saturated solutions are, from these solubilities, 3625 and 2973 cal./mole, respectively.

The normal carbonate hydrolyzes in solution to form the bicarbonate ion

$$CO_3^{=} + H_2O = HCO_3^{-} + OH^{-}$$

A correction must be applied for this hydrolysis in the various salt solutions. If x is the concentration (moles per liter) of HCO_3^- and of OH^- produced, then $(C - x)$ is the *true* concentration of the carbonate ion (from barium carbonate or strontium carbonate). Consideration of the hydrolytic equation above leads to the relation $x^2/(C - x) = K'_w/K'_2$, where K'_w is the stoichiometric ion product for water and K'_2 is the second ionization constant (stoichiometric) for carbonic acid at any particular value of the ionic strength.

Values of K'_w at 25 and 40° at different values of the ionic strength were found in the work of Harned[9] and Harned and Hamer.[10] At 25°, Harned gives values for K'_w for solutions of potassium and sodium chlorides. These values were plotted against values of the square root of the ionic strength, $\mu^{1/2}$; values of K'_w could be read off this large scale plot for any value of $\mu^{1/2}$ for both of these salts. For lithium chloride solutions, for which no K'_w data were given, the values of K'_w for sodium chloride solutions were assumed to yield data sufficiently accurate for our purposes. At 40°, Harned and Hamer gave only K'_w data for potassium chloride solutions. Again, these data were taken as sufficiently accurate for our solutions in lithium and sodium chloride solutions.

Values for K'_2 for carbonic acid at 25 and 40° (38°) were taken from the papers by MacInnes and Belcher;[11] they give empirical equations relating K'_2 and $\mu^{1/2}$ for solutions of potassium carbonate, bicarbonate and chloride. They do

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(9) Harned, This Journal, **47**, 930 (1925).

(10) Harned and Hamer, *ibid.*, **55**, 2194 (1933).

(11) MacInnes and Belcher, *ibid.*, **55**, 2630 (1933); **57**, 1685 (1935).

not give data at 40 but at 38°; these values of K_2' are *assumed* to hold at 40°.

Corrections were then applied by means of the relation $x^2/(C - x) = K'/K_2'$ for each value of "C" listed in Tables I and II and for each value of $\mu^{1/2}$. The resulting values of $(C - x)$, the true $[CO_3^=]$, were then related to the ionic strength by plotting $1/m\pm$ against $\mu^{1/2}$. Extrapolation of these curves to zero value of $\mu^{1/2}$ yielded the following values.

TABLE III

EXTRAPOLATED VALUES OF $1/m\pm$ AT $\mu^{1/2} = 0$

Salt	$BaCO_3$		$SrCO_3$	
Temp., °C.	25	40	25	40
$[1/m\pm]_{\mu=0}$	42,880	58,100	95,800	151,500

These extrapolated values of $1/m\pm$ were used to calculate the values of the activity coefficients of the carbonates in their various solutions, according to the method of Lewis and Randall,[6] by means of the relation

$$f = [1/m\pm]_\mu/[1/m\pm]_{\mu=0}$$

The following tables present these calculated values, in which "Total m" is the ionic strength.

TABLE IV

ACTIVITY COEFFICIENTS OF BARIUM CARBONATE IN ALKALI CHLORIDE SOLUTIONS

Total	Act. coeff. at 25° in			Act. coeff. at 40° in		
m	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.001	0.919	0.933	0.944	0.873	0.864	0.873
.002	.877	.909	.930	.824	.811	.823
.005	.797	.863	.901	.732	.711	.730
.010	.716	.807	.865	.633	.611	.628
.020	.581	.716	.802	.513	.492	.508
.050	.338	.501	.606	.330	.321	.356
.100	.196	.326	.415	.211	.217	.260
.200	.110	.193	.263	.119	.138	.184
.500	.056	.091	.147	.050	.076	.118
1.000	.033	.054	.098	.024	.050	.084

TABLE V

ACTIVITY COEFFICIENTS OF STRONTIUM CARBONATE IN ALKALI CHLORIDE SOLUTIONS

Total	Act. coeff. at 25° in			Act. coeff. at 40° in		
m	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.001	0.881	0.931	0.946	0.840	0.892	0.876
.002	.815	.903	.933	.761	.856	.827
.005	.690	.847	.897	.596	.784	.725
.010	.566	.783	.856	.484	.700	.614
.020	.449	.678	.783	.363	.576	.486
.050	.321	.455	.568	.236	.372	.346
.100	.238	.278	.390	.161	.229	.251
.200	.175	.149	.251	.110	.117	.177
.500	.121	.067	.159	.069	.046	.111
1.000	.089	.041	.122	.043	.025	.078

Summary

1. The solubilities at 25 and 40° of barium and strontium carbonates have been determined in pure water and in solutions of lithium, sodium and potassium chlorides. The solubilities in solutions of the alkali chlorides are presented tabularly.

2. The activity coefficients of these carbonates in the alkali chloride solutions have been calculated and recorded.

3. The average heats of solution of these carbonates into their saturated solutions have been calculated for the temperature range 25–40°.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 580]

The Magnetic Properties and Structure of Ferrihemoglobin (Methemoglobin) and Some of its Compounds

BY CHARLES D. CORYELL, FRED STITT AND LINUS PAULING

Our studies of the magnetic properties of hemoglobin derivatives containing ferrous iron,[1,2] including ferroheme, several hemochromogens, hemoglobin, and carbonmonoxyhemoglobin, led to the discovery that in two of these substances (ferroheme, hemoglobin) there are four unpaired electrons per heme, indicating that the bonds attaching the iron atoms to the rest of the molecule are essentially ionic in character, whereas the others contain no unpaired electrons, each iron atom being attached to six adjacent atoms by essentially covalent bonds. We have now investigated ferrihemoglobin[3] (acid methemoglobin), ferrihemoglobin hydroxide (alkaline methemoglobin), ferrihemoglobin fluoride, ferrihemoglobin cyanide, and ferrihemoglobin hydrosulfide, and have found a variety in magnetic properties greater than that for the ferrohemoglobin derivatives; the magnetic susceptibilities

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[1] L. Pauling and C. D. Coryell, *Proc. Nat. Acad. Sci.*, **22**, 159 (1936).

[2] L. Pauling and C. D. Coryell, *ibid.*, **22**, 210 (1936).

[3] The nomenclature used in this paper is described in ref. 2.

of ferrihemoglobin and its fluoride appear to correspond to five unpaired electrons per heme, those of the cyanide and hydrosulfide to one, and that of the hydroxide to three. The structural significance of these results is discussed in the last section of this paper.

Technique of the Magnetic Measurements.—The Gouy method was used to determine the magnetic susceptibilities of solutions of hemoglobin derivatives, the difference in susceptibility of solution and water being measured with use of a glass tube divided by a glass partition into two compartments, one containing solution and the other water.[4] The tubes used were about 18 mm. in internal diameter and 30 cm. long, and were provided with ground glass caps for the ends and with suitable supports for suspension from the balance arm. Fields of about 7640 and 8810 gausses were used; forces measured at 8810 gausses were changed to 7640 gausses by multiplication by the experimentally determined factor 0.752, and all measurements made (usually four) averaged to give a mean value of Δw (in milligrams). Measurements were made in several tubes with slightly different diameters. Each tube was calibrated by the measurement of Δw for water against air, these values being close to 47. Experimentally determined corrections have been applied for dilution and for the diamagnetism of added reagents. All susceptibility measurements were made at temperatures between 22 and 26°.

The concentration of each hemoglobin solution used was determined by reducing to ferrohemoglobin with 0.3 or 0.6 g. of sodium hydrosulfite (for 30 ml. of solution), determining Δw, then saturating with carbon monoxide in the dark or in diffuse daylight and again determining Δw. The change in Δw corresponds to a change in molal susceptibility (per heme) of $12{,}430 \times 10^{-6}$ c. g. s. u. at 24°, the effective magnetic moment of ferrohemoglobin per heme being taken[2] as 5.46 Bohr magnetons. Representing Δw for ferrohemoglobin solution by Δw_{Hb}, that for carbonmonoxyhemoglobin solution by Δw_{COHb}, and that for the solution being studied by Δw (these Δw's corresponding to the same molal concentration), the molal susceptibility (per heme) at 24° for the solution being studied is given by the equation

$$\chi_{\mathrm{molal}} = \frac{\Delta w - \Delta w_{\mathrm{COHb}}}{\Delta w_{\mathrm{Hb}} - \Delta w_{\mathrm{COHb}}} \cdot 12{,}430 \cdot 10^{-6}\ \text{c. g. s. u.} \quad (1)$$

and the effective magnetic moment per heme by the equation

$$\mu = \left(\frac{\Delta w - \Delta w_{\mathrm{COHb}}}{\Delta w_{\mathrm{Hb}} - \Delta w_{\mathrm{COHb}}}\right)^{1/2} \cdot 5.46\ \text{Bohr magnetons} \quad (2)$$

Measurements of pH values were made with a Beckman glass-electrode pH meter generously furnished by Professor A. O. Beckman of these Laboratories. As a standard 0.05 M potassium hydrogen phthalate solution, pH 3.97, was used. Corrections were applied in alkaline solutions for error due to sodium and potassium ions present as recommended by the manufacturer of the instrument.

Preparation of Ferrihemoglobin Solutions.—In the preliminary work ferrihemoglobin solutions were prepared by oxidation of oxyhemoglobin solutions with potassium ferricyanide, the excess of this reagent then being converted to ferrocyanide (which has zero magnetic moment) by the addition of sodium sulfite, which does not reduce ferrihemoglobin. It was also found that on addition to oxyhemoglobin solutions of sodium hydrosulfite and then of potassium ferricyanide the hemoglobin is oxidized to ferrihemoglobin and the excess ferricyanide reduced to ferrocyanide by the sulfite formed earlier by oxidation of the hydrosulfite by oxyhemoglobin.

In order to avoid the possibility of magnetic effects of the added iron the following very satisfactory method of preparing ferrihemoglobin solutions was developed, involving the auto-oxidation of oxyhemoglobin solutions at pH 4.8 to 5.3. Corpuscles obtained by centrifuging bovine blood are washed three times with 0.14 M potassium chloride solution, laked with ether, and centrifuged, the ether then being removed by bubbling air through the solution. To this solution enough 6 N lactic acid solution is added (about 16 ml. per liter) to bring the pH to about 4.9. At this pH the auto-oxidation reaction is complete after the solution has remained for forty-eight hours at room temperature. The solution, now at pH about 5.15, is brought to pH 7.0 by the addition with vigorous stirring of 1 N potassium hydroxide solution and centrifuged to remove the small amount of denatured protein formed during acidification. For different preparations used in this work the concentration of ferrihemoglobin, determined magnetically as described above, ranged from 0.0113 to 0.0176 formal in heme-iron.

By following the concentration of oxyhemoglobin magnetically it was found that in twenty-four hours at pH 5.2 and temperature 22° the amount of oxyhemoglobin present had fallen to 1% of its initial value;[5] in order to ensure completion of the reaction it is recommended that the solution stand for another twenty-four hours.

Ferrihemoglobin and Ferrihemoglobin Hydroxide.—The pronounced change in spectrum of ferrihemoglobin solutions accompanying change in pH from the acid to the alkaline range corresponds to the addition of hydroxyl ion to ferrihemoglobin (acid methemoglobin) to form ferrihemoglobin hydroxide (alkaline methemoglobin). Spectrophotometric studies of this reaction made by Austin and Drabkin[6] have shown that the amounts of substances present at intermediate pH values correspond closely to the equilibrium[7]

$$\mathrm{HbOH} \rightleftarrows \mathrm{Hb^+ + OH^-} \quad (3)$$

In Table I there are given magnetic data for ferrihemoglobin solutions of low ionic strength

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[4] S. Freed and C. Kasper, *Phys. Rev.*, **36**, 1002 (1930).

[5] The reaction is approximately first-order in oxyhemoglobin and first-order in hydrogen ion; the rate-determining step may be

$$\mathrm{HbO_2 + H^+ \longrightarrow Hb^+ + HO_2}$$

with the production of hydrogen superoxide. The temperature coefficient of the rate is high, about 5 for 10°.

[6] J. H. Austin and D. L. Drabkin, *J. Biol. Chem.*, **112**, 67 (1935); see also F. Haurowitz, *Z. physiol. Chem.*, **138**, 68 (1924).

[7] We use the symbol $\mathrm{Hb^+}$ to represent the amount of ferrihemoglobin containing one heme, and HbOH, Hb, $\mathrm{HbO_2}$, etc., to represent corresponding amounts of ferrihemoglobin hydroxide, ferrohemoglobin, oxyhemoglobin, etc., respectively.

in the pH range 6.7 to 12.0. The data represent experiments made with three solutions, A, B and C. Two of these, A and B, were prepared by the lactic acid auto-oxidation method described above, and the third by a similar method, hydrochloric acid being used for acidification in place of lactic acid. The results for the three solutions show no differences greater than the experimental error. The hemoglobin concentration of each solution was determined by the ferrohemoglobin–carbonmonoxyhemoglobin magnetic method.

TABLE I

MAGNETIC SUSCEPTIBILITY OF FERRIHEMOGLOBIN SOLUTIONS OF LOW IONIC STRENGTH

Solution	pH	$\chi_{\text{molal}}\cdot 10^{6}$ [a]	Solution	pH	$\chi_{\text{molal}}\cdot 10^{6}$
B	6.73	13,975	A	8.32	10,790
B	6.73	13,800	A	8.32	10,840
B	6.73	14,010	A	8.34	10,930
B	6.73	13,980	A	8.49	9,950
A	6.86	13,900	A	8.57	9,835
A	6.86	13,760	A	8.60	9,890
A	6.86	13,620	A	8.61	9,620
A	6.86	13,725	A	8.63	9,660
A	6.86	13,630	C	8.97	9,080
A	6.86	14,000	A	9.02	8,960
A	6.86	13,770	A	9.06	9,250
A	6.86	13,820	A	9.54	8,775
A	6.86	13,900	A	9.61	8,340
C	6.88	13,730	A	9.82	8,730
C	6.88	13,630	C	10.01	8,420
C	6.88	13,450	A	10.02	8,020
C	6.88	13,630	A	10.30	8,040
C	6.88	13,730	B	10.78	8,765
A	7.05	13,785	A	10.81	8,380
A	7.34	13,220	B	10.82	8,310
C	7.69	12,190	B	10.90	8,470
A	7.87	12,080	A	10.92	8,355
A	7.87	12,200	A	11.73	8,150
A	8.12	11,320			

$\chi_{\mathrm{Hb}^+}\cdot 10^6 = 14{,}060 \pm 50.$

$\chi_{\mathrm{HbOH}}\cdot 10^6 = 8350 \pm 90.$

$pK_{\mathrm{HbOH}} = 8.15 \pm 0.02.$

Ionic strength at pH 8.15 = 0.20.

[a] Paramagnetic contribution to susceptibility per mole of heme.

A portion of ferrihemoglobin solution was placed in one compartment of a tube and Δw determined. Successive small portions of potassium hydroxide solution (0.87 N) were then added with vigorous stirring, the values of pH and Δw being determined after the addition of each portion. The values of Δw were corrected for dilution and the diamagnetism of reagents, and converted into χ_{molal}, the paramagnetic contribution to the susceptibility per mole of heme, by means of equation 1. The data of Table I are shown by the open circles in Fig. 1.

The ionic strength of the hemoglobin solutions, due in part to the salts originally in solution in the erythrocytes and in part to added acid and base, changes somewhat with change in pH, the values at pH 7, 8 and 9 being about 0.17, 0.20 and 0.23, respectively. The contribution of hemoglobin to the ionic strength was ignored.

The data for these solutions represent a typical titration curve, the molal susceptibility changing rapidly over the range pH 7 to 9.5 from an asymptotic value of about $14{,}000\cdot 10^{-6}$, representing ferrihemoglobin, Hb^+, to an asymptotic value of about $8300\cdot 10^{-6}$, representing ferrihemoglobin hydroxide, HbOH. Using these estimated asymptotes to calculate concentrations of Hb^+ and HbOH, it is found that the experimental points when plotted on a graph of log $([\mathrm{Hb}^+]/[\mathrm{HbOH}])$ against pH lie close to a straight line, with slope unity to within about five per cent., showing that the reaction is first-order in hydroxyl ion, as was reported by Austin and Drabkin. A theoretical susceptibility curve was fitted to the experimental points of Fig. 1 by the following procedure. The equilibrium constant K_{HbOH} for the reaction

$$\mathrm{HbOH} \rightleftarrows \mathrm{Hb}^+ + \mathrm{OH}^-$$

is related to the mole fraction x of total ferrihemoglobin in the form Hb^+ by the equation

$$\log x/(1 - x) = pK_{\mathrm{HbOH}} - p\mathrm{H} \qquad (4)$$

in which pK_{HbOH} is log $(K_{\mathrm{HbOH}}/K_{\mathrm{W}})$, with K_{W} the equilibrium constant for the ionization of water. The value of the molal susceptibility χ as a function of pH is then given by the expression

$$\chi = x\chi_{\mathrm{Hb}} + (1 - x)\chi_{\mathrm{HbOH}} \qquad (5)$$

in which x is determined by equation 4. With χ_{HbOH}, χ_{Hb^+} and pK_{HbOH} as variable parameters, this equation was fitted to the experimental points in such a way as to minimize the mean deviation from the curve. The final curve was found to have $\chi_{\mathrm{HbOH}} = 8350 \pm 90\cdot 10^{-6}$, $\chi_{\mathrm{Hb}^+} = 14{,}060 \pm 50\cdot 10^{-6}$, and $pK_{\mathrm{HbOH}} = 8.15 \pm 0.02$, the indicated probable errors for the susceptibility values being half the mean deviations and that for pK_{HbOH} being an estimated value.

The data given in Table II and represented by the solid circles in Fig. 1 were obtained with a solution, D, to which potassium chloride had been added, the ionic strength being increased in this way to the value 1.3 (at pH 8.56). These data also are well represented by a curve corre-

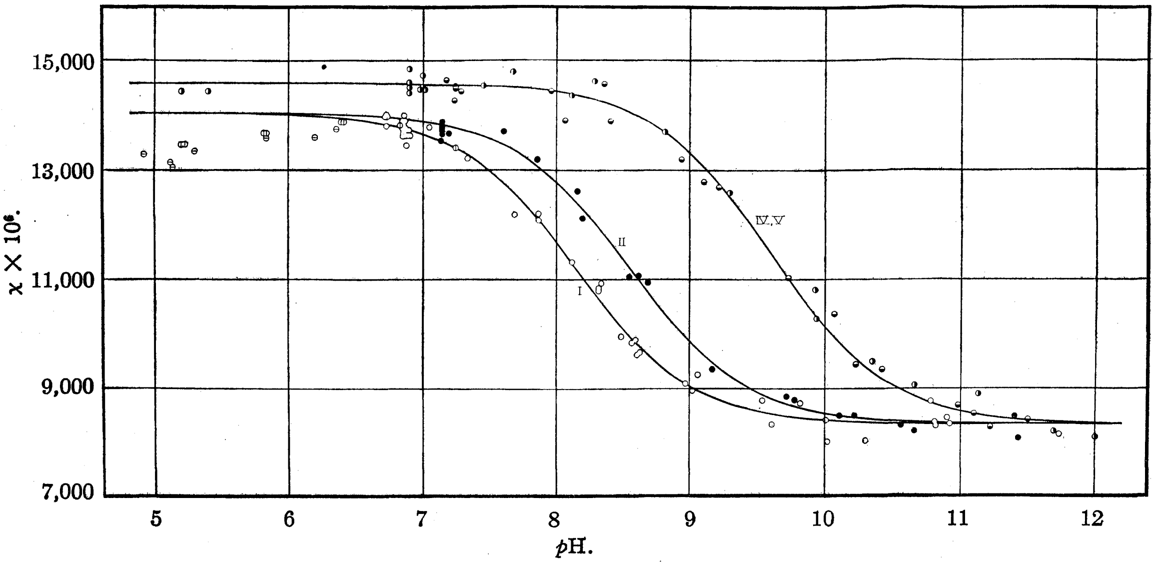

Fig. 1.—The dependence of the magnetic susceptibility of ferrihemoglobin solutions on pH: ○, solutions of low ionic strength, Table I; ●, solutions of high ionic strength, Table II; ⊖ ⦶, solutions in low pH range, Table III; ◑, solutions of low ionic strength with added fluoride, Table IV; ◒, solutions of high ionic strength, with added fluoride, Table V.

sponding to equations 5 and 4, the values of the parameters for the curve giving the best fit being $\chi_{\text{HbOH}} = 8320 \pm 60 \cdot 10^{-6}$, $\chi_{\text{Hb}^+} = 14{,}000 \pm 70 \cdot 10^{-6}$, and $pK_{\text{HbOH}} = 8.56 \pm 0.02$.

TABLE II

MAGNETIC SUSCEPTIBILITY OF FERRIHEMOGLOBIN SOLUTIONS OF HIGH IONIC STRENGTH

Solution D

pH	$\chi_{\text{molal}} \cdot 10^6$	pH	$\chi_{\text{molal}} \cdot 10^6$
7.14	13,530	8.62	11,070
7.15	13,880	8.69	10,940
7.15	13,650	9.17	9,350
7.15	13,760	9.72	8,850
7.15	13,790	9.78	8,780
7.15	13,720	10.11	8,500
7.20	13,670	10.22	8,500
7.61	13,700	10.56	8,325
7.86	13,190	10.66	8,220
8.16	12,620	11.40	8,480
8.20	12,120	11.43	8,080
8.55	11,050		

$\chi_{\text{Hb}^+} \cdot 10^6 = 14{,}000 \pm 70$.
$\chi_{\text{HbOH}} \cdot 10^6 = 8320 \pm 60$.
$pK_{\text{B}} = 8.56 \pm 0.02$.
Ionic strength at pH 8.56 = 1.3.

The values found for χ_{HbOH} and χ_{Hb^+} in solutions at high and low ionic strength are in excellent agreement. For χ_{Hb^+} we accept the average value $14{,}040 \cdot 10^{-6}$, giving double weight to the asymptote of curve I. For χ_{HbOH} we obtain the mean value $8340 \cdot 10^{-6}$ by considering in addition to the two values $8350 \cdot 10^{-6}$ and $8320 \cdot 10^{-6}$ discussed above the values $8370 \cdot 10^{-6}$ and $8320 \cdot 10^{-6}$ obtained from solutions containing fluoride ion, discussed in the following section. The structural interpretation of the susceptibility values will be considered in the concluding section of the paper.

The equilibrium constant K_{HbOH} is dependent on the ionic strength of the solution, pK_{HbOH} changing from 8.15 to 8.56 with increase in ionic strength from 0.20 to 1.3. This dependence was observed by Austin and Drabkin, who found that pK_{HbOH} could be represented approximately by the equation

$$pK_{\text{HbOH}} = \text{constant} + \alpha\sqrt{\mu} \qquad (6)$$

in which μ is the ionic strength, the value for α being about 0.6. Our measurements support this,[8] the change for curves I and II corresponding to $\alpha = 0.59$.

The value $pK_{\text{HbOH}} = 8.12 \pm 0.01$ reported by Austin and Drabkin for canine hemoglobin at ionic strength 0.10 agrees reasonably well with our value 8.15 ± 0.02 at ionic strength 0.20 (corresponding to 8.07 at ionic strength 0.10) for bovine hemoglobin; complete agreement would, of course, not be expected for hemoglobins from different species.

It has been reported by Drabkin and Austin

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(8) An experiment carried out involving the determination of change in Δw and pH for a portion of solution A, initially at pH 8.57, on the addition of successive portions of potassium chloride solution led to rough verification of the form of equation 6.

that ferrihemoglobin solutions become turbid at *p*H values less than 6. Two series of magnetic experiments were made in this *p*H range. In the first series a portion of solution A was made more and more acid by the addition, with rapid stirring, of successive small portions of 1 *N* hydrochloric acid solution, values of *p*H and Δw being determined after each acidification. These data are given in Table III and shown by the horizontally barred circles in Fig. 1. The formation of a small amount of coagulum in the acid solution was noticed; in order to eliminate possible error due to this coagulation, the following series of measurements was made. A portion of solution C was brought to *p*H 5.2 by the addition of hydrochloric acid, and centrifuged to remove the coagulum formed on acidification. The solution obtained in this way (solution E) was then made more and more alkaline by the addition of small portions of potassium hydroxide solution, values of *p*H and Δw being determined at each step. No coagulum was formed during this treatment. The ferrihemoglobin concentration, made uncertain by the loss of the coagulum resulting from the initial acidification, was determined by identifying the measured susceptibility at *p*H 7.25 (the most alkaline point) with that corresponding to the theoretical curve I. The data obtained in this way, given in Table III and represented in Fig. 1 by vertically barred circles, are in reasonably good agreement with those obtained by acidification. The measurements correspond to a decrease of about 5% in molal susceptibility in very acid solutions.

TABLE III

MAGNETIC SUSCEPTIBILITY OF FERRIHEMOGLOBIN SOLUTIONS OF LOW IONIC STRENGTH IN ACID SOLUTIONS

Solution	*p*H	$\chi_{\text{molal}}\cdot 10^6$	Solution	*p*H	$\chi_{\text{molal}}\cdot 10^6$
A	4.92	13,280	A	5.84	13,580
A	5.12	13,130	A	6.20	13,595
A	5.14	13,050	A	6.36	13,750
E	5.20	13,470	E	6.40	13,870
E	5.23	13,470	E	6.41	13,870
A	5.30	13,340	A	6.83	13,815
E	5.82	13,670	E	6.88	13,600
E	5.83	13,670	E	7.25	(13,410)

Ferrihemoglobin Fluoride.—The absorption spectrum of an acid ferrihemoglobin solution is changed in a pronounced manner by the addition of fluoride, indicating the formation of a compound. A crystalline compound was prepared and analyzed by Haurowitz,[9] who reported the substance to contain one atom of fluorine per atom of iron. Our magnetic studies have verified this, and have led to the evaluation of the equilibrium constants for the reactions

$$\mathrm{HbF} + \mathrm{OH}^- \rightleftarrows \mathrm{HbOH} + \mathrm{F}^-, \text{ and} \qquad (7)$$
$$\mathrm{HbF} \rightleftarrows \mathrm{Hb}^+ + \mathrm{F}^-$$

The data given in Tables IV (for solutions A, B, C) and V (for solution D) were obtained by adding 0.5 g. of sodium fluoride to a 32-ml. portion of ferrihemoglobin solution and adding small portions of 0.87 *N* potassium hydroxide solution, with vigorous stirring, *p*H and Δw being determined after the addition of each portion. The

TABLE IV

MAGNETIC SUSCEPTIBILITY OF FERRIHEMOGLOBIN SOLUTIONS OF LOW IONIC STRENGTH WITH ADDED FLUORIDE

Solution	*p*H	$\chi_{\text{molal}}\cdot 10^6$	Solution	*p*H	$\chi_{\text{molal}}\cdot 10^6$
A	5.2	14,430	A	8.12	14,355
C	5.4	14,430	A	8.29	14,620
A	6.90	14,620	A	8.82	13,700
A	6.90	14,510	A	9.30	12,590
A	6.90	14,410	A	9.93	10,820
A	6.90	14,845	A	9.94	10,280
B	7.0	14,730	A	10.34	9,500
B	7.0	14,520	A	10.66	9,060
C	7.0	14,480	A	11.13	8,900
C	7.0	14,480	A	11.69	8,210
A	7.46	14,530	A	12.0	8,115
A	7.68	14,790			

$\chi_{\text{HbF}}\cdot 10^6$ = 14,630 ± 70 (uncorr.), 14,660 ± 70 (corr.).
$\chi_{\text{HbOH}}\cdot 10^6$ = 8370 ± 140.
$pK_{\text{OH,F}}$ = 9.63 ± 0.01 (uncorr.), 9.65 ± 0.01 (corr.).
Ionic strength at *p*H 9.63 = 0.54.
$[\mathrm{F}^-]$ = 0.34 at *p*H 9.63.

TABLE V

MAGNETIC SUSCEPTIBILITY OF FERRIHEMOGLOBIN SOLUTIONS OF HIGH IONIC STRENGTH WITH ADDED FLUORIDE

Solution D

*p*H	$\chi_{\text{molal}}\cdot 10^6$	*p*H	$\chi_{\text{molal}}\cdot 10^6$
7.18	14,640	9.11	12,780
7.24[a]	14,270	9.22	12,680
7.25	14,490	9.73	11,030
7.25	14,520	10.07	10,360
7.29	14,430	10.23	9,440
7.96	14,430	10.42	9,350
8.07	13,900	10.98	8,690
8.36[b]	14,570	11.10	8,530
8.41	13,880	11.22	8,290
8.94[a]	13,190	11.50	8,425

$\chi_{\text{HbF}}\cdot 10^6$ = 14,500 ± 80 (uncorr.), 14,550 ± 80 (corr.).
$\chi_{\text{HbOH}}\cdot 10^6$ = 8320 ± 40.
$pK_{\text{OH,F}}$ = 9.60 ± 0.01 (uncorr.), 9.64 ± 0.01 (corr.).
Ionic strength at *p*H 9.60 = 1.6.
$[\mathrm{F}^-]$ = 0.34 at *p*H 9.60.

[a] By adding 1 *N* HCl to solution of *p*H 10.98. [b] By adding 1 *N* HCl to solution of *p*H 9.22.

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[9] F. Haurowitz, *Z. physiol. Chem.*, **138**, 68 (1924).

points for solutions A, B and C, with low ionic strength (0.54 at pH 9.6), and those for solution D, with high ionic strength (1.6 at pH 9.6), lie close to the same curve, showing that there is no appreciable salt effect for the reaction. This provides support for the postulate that the reaction consists essentially in the conversion of ferrihemoglobin fluoride into ferrihemoglobin hydroxide (eq. 7), for which no appreciable salt effect would be expected. Further evidence for equation 7 will be mentioned later.

The molal susceptibility values of Tables IV and V can be approximated closely by curves of the type used above for the ferrihemoglobin–ferrihemoglobin hydroxide equilibrium. For reaction 7 the equilibrium constant $K_{\mathrm{OH,F}}$ has the value

$$K_{\mathrm{OH,F}} = [\mathrm{HbOH}][\mathrm{F}^-]/[\mathrm{HbF}][\mathrm{OH}^-] \qquad (9)$$

and the molal susceptibility is given by the equation

$$\chi = y\chi_{\mathrm{HbF}} + (1 - y)\chi_{\mathrm{HbOH}} \qquad (10)$$

in which y is the mole fraction of total ferrihemoglobin in the form of ferrihemoglobin fluoride, given by the equation

$$\log y/(1 - y) = pK_{\mathrm{OH,F}} - p\mathrm{H} \qquad (11)$$

in which $pK_{\mathrm{OH,F}}$ is $-\log (K_{\mathrm{OH,F}}K_{\mathrm{W}}/[\mathrm{F}^-])$. The asymptotes of the curves which fit the data most closely are $14{,}630 \cdot 10^{-6}$ and $8{,}370 \cdot 10^{-6}$ for solutions A, B and C, and $14{,}500 \cdot 10^{-6}$ and $8320 \cdot 10^{-6}$ for solution D. The values $8370 \cdot 10^{-6}$ and $8320 \cdot 10^{-6}$, representing χ_{HbOH}, are in excellent agreement with the values $8350 \cdot 10^{-6}$ and $8320 \cdot 10^{-6}$ found for solutions without added fluoride.

The values for the other asymptote represent molal susceptibility not of ferrihemoglobin fluoride itself but of ferrihemoglobin fluoride containing a small fraction of ferrihemoglobin (Hb^+). From the equilibrium constants given below the values of the concentration ratio $[\mathrm{Hb}^+]/[\mathrm{HbF}]$ are found to be 0.047/0.953 for solutions A, B and C, and 0.094/0.906 for solution D. Using these ratios and the known value of χ_{Hb^+} to correct for the ferrihemoglobin present, the values $\chi_{\mathrm{HbF}} = 14{,}660 \pm 70 \cdot 10^{-6}$ and $14{,}550 \pm 80 \cdot 10^{-6}$ are obtained; we accept for χ_{HbF} the mean of these closely agreeing values, $14{,}610 \cdot 10^{-6}$.

The values 9.63 and 9.60 for $pK_{\mathrm{OH,F}}$ given by the curves lead on similar consideration of the $[\mathrm{Hb}^+]/[\mathrm{HbF}]$ ratio to the corrected values 9.65 and 9.64, which agree to within their estimated probable error of 0.01. Introducing the values of $[\mathrm{F}^-]$ (0.34 at pH 9.6) and K_{W} ($10^{-14.01}$), we obtain for the equilibrium constant $K_{\mathrm{OH,F}}$ at 24° the value $0.78 \cdot 10^4$.

The equilibrium constant K_{HbOH} for reaction 3 is given by the equation

$$\log K_{\mathrm{HbOH}} = -6.12 + 0.59\sqrt{\mu} \qquad (12)$$

Combining with this the value of $K_{\mathrm{OH,F}}$, we obtain for K_{HbF}, the equilibrium constant for the reaction

$$\mathrm{HbF} \rightleftarrows \mathrm{Hb}^+ + \mathrm{F}^- \qquad (13)$$

the expression

$$\log K_{\mathrm{HbF}} = -2.23 + 0.59\sqrt{\mu} \qquad (14)$$

Three sets of measurements were made to test these equilibrium constants by direct titration with potassium fluoride solution. In the first run a portion of solution A was brought to pH 8.60, and values of pH and Δw were measured after the addition of successive small portions of known volume of 2.00 f potassium fluoride solution. The average of nine values of K_{HbF} corresponding to the nine added portions of fluoride solution is 0.0145, with a mean deviation of 0.0012; this value is in good agreement with the value 0.013 given by equation 14 for $\mu = 0.34$. When the formality of fluoride in the solution had reached 0.28, the pH was observed to have changed to the value 8.89, an increase of 0.29; this agrees well with the calculated change in pH expected because of the replacement of hydroxyl in ferrihemoglobin hydroxide by fluorine, 0.30. A less reliable set of six measurements made on solution D at pH 8.6 gave the average value 0.049 for K_{HbF}. This is somewhat larger than the value 0.029 given by equation 14 for $\mu = 1.4$, perhaps because of experimental error, the total change in Δw values during the run being less than 1 mg. A set of five measurements made on solution A at pH 6.2 gave for K_{HbF} the average value 0.008, somewhat lower than the value 0.010 expected for $\mu = 0.22$; the difference may be due to error in the measurement of Δw, which changed by only 0.40 mg. during the run.

A determination of the value of K_{HbF} by a spectrophotometric method has been reported by Lipmann.[10] The value found, about 0.015, for a solution of swine hemoglobin of uncertain ionic strength agrees with that calculated from equation 14 with μ given the reasonable value 0.5. Lipmann also reported a decrease of the constant in very acid solutions.

Ferrihemoglobin Cyanide.—Crystalline ferrihemoglobin cyanide was first obtained by Zey-

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[10] F. Lipmann, *Biochem. Z.*, **206**, 171 (1929).

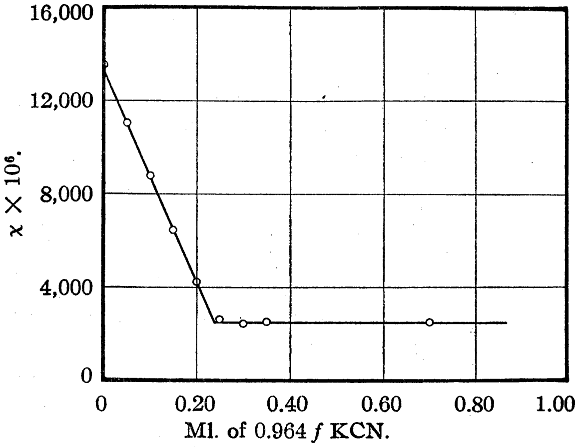

Fig. 2.—The magnetic titration of ferrihemoglobin with potassium cyanide at pH 6.75.

nek,[11] who by analysis showed the substance to contain one cyanide per heme. We have verified this by titration of a ferrihemoglobin solution with cyanide. The data represented in Fig. 2 were obtained with a solution containing equal volumes of ferrihemoglobin solution B and a phosphate buffer, the pH of the solution being 6.75. To 31.25 ml. of this solution there was added from a 1-ml. glass syringe graduated in hundredths successive measured volumes (0.050 ml.) of 0.964 *f* potassium cyanide solution. When the molal susceptibility is plotted against the amount of cyanide added the first five points fall close to a straight line and the last four to a horizontal straight line. The intersection of these lines occurs at 0.235 ml., which agrees to within the experimental error with the value 0.236 ml. calculated for one cyanide per heme. The value found for χ_{HbCN} in this experiment is $2520 \cdot 10^{-6}$. A similar experiment performed at pH 10.8 gave similar results.

In order to determine the molal susceptibility of ferrihemoglobin cyanide accurately sets of duplicate measurements were made with unbuffered solution B at pH 6.7 and with solution B brought to pH 10.9 by the addition of potassium hydroxide solution, an excess of potassium cyanide solution being added in each case. The values found for $\chi_{HbCN} \cdot 10^6$ are 2590 and 2620 at pH 6.7 and 2630 and 2590 at pH 10.9. There is accordingly no dependence of χ_{HbCN} on pH. The average of the measured values is $2610 \cdot 10^{-6}$. Values approximating this were also obtained in several preliminary measurements and in measurements made incidental to other experiments.

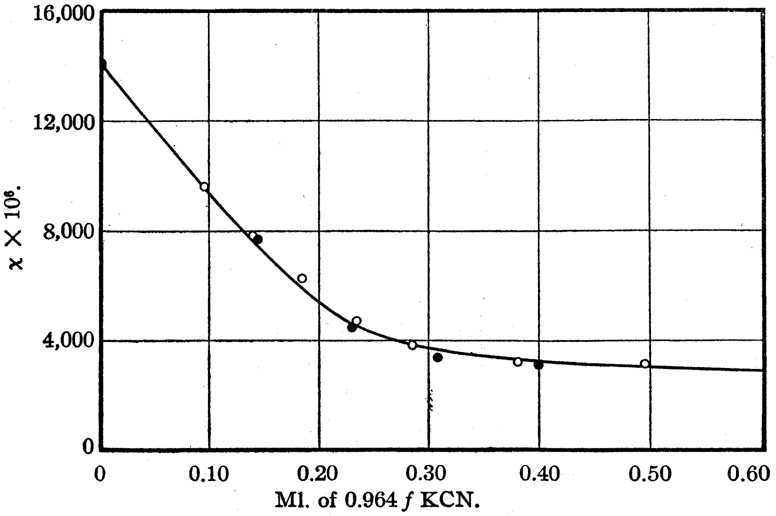

Fig. 3.—The magnetic titration of ferrihemoglobin with potassium cyanide at pH 4.77.

In order to obtain an approximate value for the equilibrium constant K_{HbCN} for the reaction

$$HbCN \rightleftarrows Hb^+ + CN^- \qquad (15)$$

two cyanide titration experiments were made with ferrihemoglobin solution B brought to pH 4.77 by the addition of an equal volume of an acetate buffer solution 2 *M* in acetic acid and 2 *M* in sodium acetate. A portion of the solution was placed in one compartment of a tube, which was then closed with a thin rubber stopper. Portions of 0.964 *f* potassium cyanide solution were then added by means of a syringe, the needle being inserted through the rubber stopper, and Δw values were measured. The corresponding values of χ_{molal} for the two runs are shown in Fig. 3. When about one-half of the stoichiometric amount of cyanide has been added it is almost entirely in the form of HbCN. With larger amounts of cyanide the formation of HbCN is incomplete, the amount of cyanide present as HCN becoming appreciable. The ratio $[CN^-]/[HCN]$ is about 10^{-4}, so that the equilibrium measured is essentially

$$Hb^+ + HCN \rightleftarrows HbCN + H^+ \qquad (16)$$

The experimental points lie close to the theoretical equilibrium expression, represented by the curve in Fig. 3; the value found for the corresponding

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[11] R. v. Zeynek, *Z. physiol. Chem.*, **33**, 426 (1901).

equilibrium constant (presumably essentially independent of ionic strength) is 18. This value multiplied by the ionization constant of HCN, $2.0 \cdot 10^{-9}$, gives for K_{HbCN} the value $3.6 \cdot 10^{-8}$, at zero ionic strength.[12] The dependence on ionic strength is probably nearly the same as for K_{HbOH} and K_{HbF}; we hence write for K_{HbCN} the equation

$$\log K_{\text{HbCN}} = -7.44 + 0.59\sqrt{\mu} \qquad (17)$$

Ferrihemoglobin Hydrosulfide.—It was discovered by Keilin[13] that ferrihemoglobin forms a compound with hydrogen sulfide,[14] containing one sulfur atom per heme. By analogy with other compounds of ferrihemoglobin we consider it likely that this compound is ferrihemoglobin hydrosulfide, HbSH.

Solutions of ferrihemoglobin hydrosulfide made by addition of sodium hydrosulfide to ferrihemoglobin solution buffered to *p*H values in the range 5 to 7 were found to decompose rapidly, apparently undergoing auto-reduction to ferrohemoglobin, as shown by its spectrum and molal susceptibility and by the spectrum (that of oxyhemoglobin) observed after air is admitted to the solution. In order to evaluate χ_{HbSH} the following experiments were performed. To a portion of ferrihemoglobin solution B an equal volume of acetate or phosphate buffer was added. About 30 ml. of the solution was then placed in a compartment of a tube, which was closed with a thin rubber stopper, and 0.5 ml. (or, in one experiment, 0.1 ml.) of 4 *f* sodium hydrosulfide solution was added through the stopper with a syringe. The tube was then placed in position, and readings of Δw were taken at intervals of about two minutes, the first being made about six minutes after the addition of the hydrosulfide. The measured values of Δw correspond to a rapid increase of the molal susceptibility with time, χ being at first linear in t and then approaching an asymptote. The data are represented by the theoretical expression for a reaction first order with respect to HbSH, with the asymptotic value of χ_{molal} equal to that for ferrohemoglobin. To evaluate χ_{HbSH} the susceptibility values over the nearly linear portion of the curve were extrapolated to zero time; for four solutions, with *p*H 5.1, 5.7, 5.7, and 7.0, respectively, the values 2240, 2110, 2260 and 1930.10^{-6}, average $2140 \cdot 10^{-6}$, were obtained. A value for the dissociation constant of the substance is not provided by our data.[15]

The rate constant $k = -\text{d}(\ln[\text{HbSH}])/\text{d}t$ has the approximate value $5 \cdot 10^{-3}$ (with t measured in minutes), the observed values of $k \cdot 10^3$ being 5.0 at *p*H 5.08, 12.0 at *p*H 5.73, 5.2 at *p*H 7.02, and 3.0 at *p*H 5.73. (The third experiment was made with phosphate buffer, the others with acetate buffers; the fourth was made with 0.1 ml., the others with 0.5 ml. of 4 *f* sodium hydrosulfide solution added.) It is seen that no more than about 2-fold variation was observed over the *p*H range 5.1 to 7.0, and that the rate seems to increase with increase in the concentration of hydrosulfuric acid.

The Interpretation of the Molal Susceptibility Values

The values of the paramagnetic part of the molal susceptibility (per heme) at 24° of the substances studied in this investigation are collected in Table VI. If it be assumed that these values result from the independent orientation of the magnetic moments of the hemes and that Curie's law is applicable, they correspond to the values of the magnetic moment μ, in Bohr magnetons, shown in the last column of the table, calculated with the equation

$$\mu = 2.84\sqrt{\chi_{\text{molal}}T}$$

in which T is the absolute temperature.

TABLE VI

VALUES OF THE PARAMAGNETIC MOLAL SUSCEPTIBILITY AND EFFECTIVE MAGNETIC MOMENT (PER HEME) OF FERRIHEMOGLOBIN AND SOME OF ITS COMPOUNDS

	$\chi_{\text{molal}} \cdot 10^{6\,a}$	μ^b
Ferrihemoglobin, Hb^+	14,040	5.80
Ferrihemoglobin hydroxide, HbOH	8,340	4.47
Ferrihemoglobin fluoride, HbF	14,610	5.92
Ferrihemoglobin cyanide, HbCN	2,610	2.50
Ferrihemoglobin hydrosulfide, HbSH	2,140	2.26

[a] At 24°. [b] In Bohr magnetons.

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[12] An effort to check this result was made by determining magnetically the ratio ferrihemoglobin–ferrihemoglobin cyanide in a solution in equilibrium with solid silver cyanide and solid silver chloride. Three measurements, made with concentrations 0.20, 0.43 and 1.00 *f* of chloride ion, gave for the ratio $[\text{Hb}^+]/[\text{HbCN}]$ the values 0.20, 0.093 and 0.040, respectively. Taking $1.7 \cdot 10^{-10}$ as the solubility product of AgCl and $7 \cdot 10^{-15}$ as that of AgCN [as given by M. Randall and J. O. Halford, THIS JOURNAL, **52**, 178 (1930)], these measurements lead to $K_{\text{HbCN}} = 1.6 \cdot 10^{-6}$, in rather poor agreement with the value $1 \cdot 10^{-7}$ given by equation 17. It is possible that the disagreement is due to error in the solubility product of AgCN, inasmuch as an older value $4.5 \cdot 10^{-17}$ [Bodländer and Eberlein, *Z. anorg. Chem.*, **39**, 197 (1904)] leads to $K_{\text{HbCN}} = 1 \cdot 10^{-8}$.

[13] D. Keilin, *Proc. Roy. Soc.* (London), **B113**, 393 (1933).

[14] Keilin emphasized the fact that this compound is different from the green substance formed from ferrohemoglobin in the presence of hydrogen sulfide and oxygen.

[15] Keilin performed experiments to determine this dissociation constant. No mention of the auto-reduction reaction which we observed is made in his paper.

The possibility should be considered that the moments of the four hemes in a molecule of molecular weight 68,000 are not oriented independently, but instead are combined to a resultant constant moment for the molecule, with magnitude twice that given for μ in the table. This possibility was discussed in connection with ferrohemoglobin,[2] and reasons were advanced for rejecting it in favor of the alternative simple interpretation in terms of hemes which interact with one another only weakly; it was suggested that the observed effective moment per heme for ferrohemoglobin, 5.46, is somewhat larger than the expected value for four unpaired electrons (spin moment alone, 4.90; expected orbital contribution, about 0.1 to 0.4) because of a partial stabilization of parallel orientations of the heme moments through heme–heme interaction. Some of the arguments advanced in support of this interpretation for ferrohemoglobin are applicable to ferrihemoglobin and its compounds also, and we have, moreover, been able to interpret the susceptibility values in a reasonably satisfactory manner on this basis and not on the basis of constant moments for the four-heme molecules; hence we believe that in these substances too the heme moments are entirely or almost entirely independent of one another.[16]

The effective moment per heme observed for ferrihemoglobin fluoride is 5.92, which is identical with the theoretical spin moment for five unpaired electrons, 5.917. Moreover, for five unpaired *d* electrons the total moment is equal to the spin moment, the orbital contribution vanishing because of the occupancy of each orbit in the subgroup by one electron; there is actually very close agreement between the theoretical spin moment and the experimental values for iron-group ions and complexes with five unpaired electrons, representative observed moments being 5.94 for Mn^{++} and 5.86–5.98 for Fe^{+++} in aqueous solution, 5.88 for the fluoferriate complex $[FeF_6]^{\equiv}$, and 5.91 for the complex $[FeF_5 \cdot H_2O]^{=}$. The observed moment for ferrihemoglobin fluoride shows that in this substance, as in the fluoferriate complex, the bonds from iron to the surrounding atoms (fluorine, the four porphyrin nitrogens, one globin nitrogen atom) are essentially ionic in character.

The effective moment per heme for ferrihemoglobin itself, 5.80, shows that in this complex too the bonds from the iron atom to the surrounding atoms are essentially ionic. It is possible that the coördination number of iron is here only five; it seems to us probable, however, that the sixth octahedral position is occupied by a water molecule,[17] the complex being $[HbOH_2]^+$ rather than Hb^+. The transition to ferrihemoglobin hydroxide would then involve loss of a proton (with change in bond type—*v. infra*) rather than addition of an hydroxyl ion.

The difference[18] between the observed moment 5.80 and the theoretical value 5.92 we attribute to heme–heme interaction operating to stabilize configurations in which the heme moments are opposed. Why the interaction should decrease the effective moment of ferrihemoglobin, increase that of ferrohemoglobin, and leave that of ferrihemoglobin fluoride unchanged we do not know.

The observed decrease in susceptibility (by about 5%) of ferrihemoglobin solutions in the low *p*H range may be due to change in the heme–heme interactions. Further experimental data are needed before a reliable explanation of this phenomenon can be given.[19]

The susceptibilities of ferrihemoglobin cyanide and ferrihemoglobin hydrosulfide correspond to the effective heme moments 2.50 and 2.26, respectively. These are close to the value expected for one unpaired electron (1.732 plus an orbital contribution of 0.3 to 0.5), showing that in these molecules two *d* orbitals of each iron atom are involved in covalent bond formation. Without doubt the structures are similar to that of the ferricyanide ion[20] (with $\mu = 2.33$), the iron atom being attached by essentially covalent bonds to six surrounding atoms arranged octahedrally, consisting of the four porphyrin nitrogens, one globin nitrogen, and the carbon of cyanide or sulfur of hydrosulfide. The observed moments

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[16] The possibility that the moments of the hemes in pasri are combined to constant resultants also seems unlikely to us.

[17] It is of interest that one fluorine in $[FeF_6]^{\equiv}$ is easily replaced by a water molecule, forming $FeF_5 \cdot H_2O^{=}$.

[18] The reality of the difference is shown by the directly observed increase in susceptibility of ferrihemoglobin solution on the addition of fluoride.

[19] During the cyanide titrations it was observed that in solutions heavily buffered (with acetate) at *p*H 4.8 the molal susceptibility of ferrihemoglobin has the value $14,020 \cdot 10^{-6}$, which agrees well with the asymptotic value given by the curves rather than with the values observed for unbuffered solutions.

[20] We have made a determination of the molal susceptibility of potassium ferricyanide in solution by the differential method, the diamagnetic correction being made by using the susceptibility of the ferrocyanide solution obtained by reduction with sodium sulfite. Five measurements made at concentrations of 0.608 and 0.304 *f* gave for the paramagnetic molal susceptibility at 22.0° the value $2280 \pm 10 \cdot 10^{-6}$, corresponding to $\mu = 2.33 \pm 0.01$ Bohr magnetons.

are somewhat higher than expected, indicating some heme–heme interaction; it is possible, on the other hand, that the orbital contribution is greater than usual.

None, or one, or two of the $3d$ orbitals of trivalent iron atom in a complex may be involved in covalent bond formation, the number of unpaired electrons being five, three, or one, respectively, and the moment 5.92, about 4.2, or about 2.0 Bohr magnetons. Many complexes of the first type and many of the third type are known, whereas iron complexes of the intermediate type are very rare.[21] Ferrihemoglobin hydroxide apparently is of this type; the observed effective moment 4.47 is only slightly larger than that expected for three unpaired electrons (spin moment 3.88, orbital contribution about 0.4).

The nature of the bonds in this complex is somewhat uncertain, since, although the value of the magnetic moment is that which is associated with square coördination (as in nickel protoporphyrin[1]), there is little doubt that the configuration about the iron atom is octahedral. Four dsp^2 covalent bonds directed to the corners of a square would utilize one d orbital; in ferrihemoglobin hydroxide it is probable that these four covalent bonds resonate among the six adjacent atoms, each of which is then attached to the iron atom by a bond with roughly two-thirds covalent character (or perhaps somewhat less).

Summary

Magnetic measurements at approximately 24° of solutions of ferrihemoglobin and some of its compounds have been made, leading to values of the paramagnetic part of the molal susceptibility which correspond to the following values of the effective magnetic moment per heme, in Bohr magnetons: ferrihemoglobin, 5.80; ferrihemoglobin hydroxide, 4.47; ferrihemoglobin fluoride, 5.92; ferrihemoglobin cyanide, 2.50; ferrihemoglobin hydrosulfide, 2.26. For ferrihemoglobin and its fluoride these correspond to five unpaired electrons per heme, indicating essentially ionic bonds; for the cyanide and hydrosulfide to one, indicating essentially covalent bonds; and for the hydroxide to three, indicating bonds of an intermediate type.

Values determined by magnetic titrations are reported for the dissociation constants of ferrihemoglobin hydroxide, fluoride and cyanide.

PASADENA, CALIF. RECEIVED FEBRUARY 8, 1937

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[21] Measurements of χ made by L. Cambi and A. Cagnasso, *Rend. Ist. Lombardo Sci.*, **67**, 741 (1934), for complexes of $Fe(CNS)_2$ and $Co(CN)_2$ with *o*-phenanthroline and 2,2′-bipyridyl indicate structures of this type.

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

Arsonated Derivatives of Mixed Ketones

BY ROBERTA ELEANOR OMER AND CLIFF S. HAMILTON

In a study of arsonated aliphatic–aromatic ketones[1–4] a number of attempts were made to condense *p*-hydroxyphenylarsonic acid with nitriles in various solvents with and without catalysts. There was no evidence of condensation in any case, results which were not entirely unexpected in view of the fact that the literature does not report condensations with nitrophenols and hydroxybenzenesulfonic acids.

Although direct arsonation of resorcinol[5] gives good yields of resorcinol arsonic acid, 2,4-dihydroxyacetophenone[6] and the corresponding propiophenone derivative did not react with arsenic acid to form more than traces of the arsonic acids. Protection of the phenolic hydroxyl groups by acetylation[7] or methylation[8] before heating with arsenic acid failed to give any arsonic acid although a few instances of direct arsonation of compounds containing no free hydroxyl groups are recorded.[5] Methylation of the products before their separation from the reaction mixture gave 10% yields.

The introduction of arsenic into hydroxyaromatic–aliphatic ketones through the diazo reaction[9] was exceedingly difficult. Attempts to condense *p*-nitrophenol and nitroresorcinol[10] with

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[1] Lewis and Cheetham, THIS JOURNAL, **43**, 2117 (1921).

[2] Lewis and Cheetham, *ibid.*, **45**, 510 (1923).

[3] Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, Austrian Patent 100,211 (1922).

[4] Margulies, British Patent 220,668 (1923).

[5] Bauer, *Ber.*, **48**, 509 (1915).

[6] Hoesch, *ibid.*, **48**, 1122 (1915).

[7] Brüll and Friedlaender, *ibid.*, **30**, 297 (1897).

[8] Perkin, Robinson and Turner, *J. Chem. Soc.*, **93**, 1085 (1908).

[9] Bart, *Ann.*, **429**, 55 (1922).

[10] Kauffmann and Kügel, *Ber.*, **44**, 753 (1911).

nitriles proving unsuccessful, it was found necessary to prepare the amines of the hydroxy ketones for use in the diazotization from 2,4-dihydroxyacetophenone and the corresponding propiophenone derivative by nitration and reduction of the nitro compounds. The instability of the resulting amines required their isolation as amine hydrochlorides. The same sort of difficulty was encountered in arsonation through the diazo reaction as in direct arsonation. Both 2,4-dihydroxy-5-aminoacetophenone and 2,4-dihydroxy-5-aminopropiophenone were easily diazotized; but, under the wide variety of conditions tried, no more than a very small amount of an unstable impure material showing arsonation could be obtained.

However, methylation of the hydroxyl groups in 2,4-dihydroxy-5-nitroacetophenone and the corresponding propiophenone derivative resulted in very stable compounds. These were reduced catalytically and the somewhat unstable amines isolated through their hydrochlorides. Arsonation of these compounds proceeded easily, giving good yields of 2,4-dimethoxy-5-arsonoacetophenone and 2,4-dimethoxy-5-arsonopropiophenone.

Experimental

2,4-Dihydroxypropiophenone.[11,12]—Prepared from resorcinol and propionitrile by a method similar to that used by Hoesch in making 2,4-dihydroxyacetophenone[6]; yield 65%.

2,4-Dimethoxypropiophenone.—From 2,4-dihydroxypropiophenone following the method of Perkin, Robinson and Turner.[8] The yellow oily solid thus obtained was recrystallized twice from 50% ethyl alcohol solution, giving a white solid with a pleasant ethereal odor; m. p. 67°; 68% yield.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.00; H, 7.21. Found: C, 67.93, 67.76; H, 7.22, 7.21.

2,4-Dihydroxy-5-nitroacetophenone.—Fifty grams of 2,4-dihydroxyacetophenone was added in small portions with constant stirring to 400 cc. of nitric acid (1.42) cooled in an ice-bath. The addition was carried on at such a rate that each portion of the solid was dissolved completely before the next was introduced and so that the temperature remained below 10°. The stirring was continued for an hour, during which time a dark red solid separated, and the mixture then poured into a 2-liter beaker half full of chipped ice. The nitro compound was filtered out, washed with water and boiled with 500-cc. portions of water until all of the red color had been removed. The light yellow solid was then filtered out, dried and recrystallized from ethyl alcohol, giving 46 g. of the mononitro derivative; m. p. 142°.

Anal. Calcd. for $C_8H_7O_5N$: N, 7.11. Found: N, 7.13, 7.12.

2,4-Dihydroxy-5-nitropropiophenone.—Nitration of 2,4-dihydroxypropiophenone by a procedure similar to that used with the corresponding acetophenone derivative gave a 77% yield of the white nitro compound; m. p. 131°.

Anal. Calcd. for $C_9H_9O_5N$: N, 6.64. Found: N, 6.68, 6.66.

2,4-Diacetoxy-5-nitropropiophenone.—From 2,4-dihydroxy-5-nitropropiophenone by the method of Brüll and Friedlaender.[7] Recrystallization from carbon tetrachloride gave a 90% yield of the cream colored product; m. p. 89°.

Anal. Calcd. for $C_{13}H_{13}O_7N$: N, 4.98. Found: N, 5.04, 4.92.

2,4-Dimethoxy-5-nitroacetophenone.—Nineteen and seven-tenths grams of 2,4-dihydroxy-5-nitroacetophenone was dissolved in 33 cc. of 20% sodium hydroxide solution. To this solution in a 250-cc. flask was added 30 cc. of dimethyl sulfate. The mixture was stirred thoroughly, heated gently until the strongly exothermic reaction started and shaken until cool. The solid brown cake which formed was filtered out and ground up in *N* sodium carbonate solution to remove any material not entirely methylated. The solid remaining was filtered out, washed thoroughly with water, dried and recrystallized from hot ethyl alcohol; yield 15.5 g. of a finely divided cream colored product; m. p. 177°.

Anal. Calcd. for $C_{10}H_{11}O_5N$: N, 6.22. Found: N, 6.32, 6.25.

2,4-Dimethoxy-5-nitropropiophenone.—By a procedure similar to that used with 2,4-dihydroxy-5-nitroacetophenone, a 75% yield of cream colored dimethoxy derivative, m. p. 155°, was obtained.

Anal. Calcd. for $C_{11}H_{13}O_5N$: N, 6.70. Found: N, 6.64, 6.81.

Amine Hydrochlorides

General Procedure.—The hydrochloride of the amine was prepared from the corresponding nitro compound by catalytic reduction[13] in acetone solution using Raney catalyst.[14] At the end of the reaction the catalyst was filtered out, half the acetone removed by distillation under reduced pressure, and the hydrochloride prepared by passing dry hydrogen chloride into the remaining solution. In cases where the hydrochloride was somewhat soluble in acetone, ether was added to throw it out. The amine hydrochloride was filtered out, dried and recrystallized from

TABLE I

Hydrochloride of	Formula	Nitrogen analyses, % Calcd.	Found	
2,4-Dihydroxy-5-amino-acetophenone	$C_8H_{10}O_3NCl$	6.88	6.68	6.77
2,4-Dihydroxy-5-amino-propiophenone	$C_9H_{12}O_3NCl$	6.44	6.31	6.33
2,4-Dimethoxy-5-amino-acetophenone	$C_{10}H_{14}O_3NCl$	6.05	5.95	5.92
2,4-Dimethoxy-5-amino-propiophenone	$C_{11}H_{16}O_3NCl$	5.70	5.61	5.60

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[11] Nencki and Schmid, *J. prakt. Chem.*, **23**, 546 (1881).

[12] Brewster and Harris, THIS JOURNAL, **52**, 4866 (1930).

[13] Stevinson and Hamilton, THIS JOURNAL, **57**, 1298 (1935).

[14] Raney, U. S. Patent 1,628,190 (1927).

alcohol, giving nearly quantitative yields of finely divided solid which was not melted at 300°.

Amines

General Procedure.—The amines were prepared from the corresponding amine hydrochlorides by addition of *N* sodium carbonate solution.

TABLE II

	M. p., °C.	Formula	Nitrogen analyses, % Calcd.	Found	
2,4-Dihydroxy-5-amino-acetophenone	137–142[a]	$C_8H_9O_3N$	8.38	8.19	8.21
2,4-Dihydroxy-5-amino-propiophenone	147–151[a]	$C_9H_{11}O_3N$	7.74	7.58	7.61
2,4-Dimethoxy-5-amino-acetophenone	114	$C_{10}H_{13}O_3N$	7.18	7.34	7.28
2,4-Dimethoxy-5-amino-propiophenone	107	$C_{11}H_{15}O_3N$	6.70	6.84	6.81

[a] With decomposition.

2,4 - Dimethoxy - 5 - arsonoacetophenone.—(a) 2,4 - Dimethoxy-5-arsonoacetophenone was prepared from the hydrochloride of 2,4-dimethoxy-5-aminoacetophenone by diazotization followed by coupling with sodium arsenite. Twenty-three and a half grams of the amine hydrochloride was dissolved in water and 16.5 cc. of 12 *N* hydrochloric acid added. This was cooled to 0° and diazotized by adding slowly 105 cc. of *N* sodium nitrite solution. The resulting solution was stirred for an additional fifteen minutes, cooled, and 20 cc. of 5 *N* sodium hydroxide solution stirred in, followed at once by a mixture containing 75 cc. of 2 *N* disodium monohydrogen arsenite solution, 2.5 cc. of 12 *N* hydrochloric acid, 200 cc. of water, 200 cc. of ice and 40 cc. of 10% copper sulfate solution. Nitrogen was evolved rapidly, and a few cc. of ethyl acetate was added to prevent excessive foaming. The reaction mixture was stirred for three hours, and, after standing overnight, it was heated to 50–60° on a steam-bath and filtered. The filtrate was made acid to litmus with acetic acid and concentrated to half its former volume on a steam-bath. The mixture was filtered twice through a charcoal filter to remove the color. On making the filtrate acid to Congo red paper with hydrochloric acid, the white arsonic acid separated. It was filtered out, washed, dried and purified by recrystallizing twice from "cellosolve"; yield 17 g.; m. p. 250°.

(b) Methylation of the reaction mixture obtained on heating 2,4-dihydroxyacetophenone and arsenic acid for five hours at 150–155° gave a 7% yield of 2,4-dimethoxy-5-arsonoacetophenone.

Anal.[15] Calcd. for $C_{10}H_{13}O_6As$: As, 24.35. Found: As, 24.30, 24.32.

2,4-Dimethoxy-5-arsonopropiophenone.—(a) A 61% yield of 2,4-dimethoxy-5-arsonopropiophenone was obtained from 2,4-dimethoxy-5-aminopropiophenone through the diazo reaction and coupling with sodium arsenite; m. p. 243°. (b) Methylation of the reaction mixture from the direct arsonation of 2,4-dihydroxypropiophenone by heating with arsenic acid for seventy-five hours at 100° gave an 11% yield of 2,4-dimethoxy-5-arsonopropiophenone.

Anal. Calcd. for $C_{11}H_{15}O_6As$: As, 23.55. Found: As, 23.42, 23.44.

Summary

1. 2,4-Dimethoxy-5-arsonoacetophenone and 2,4-dimethoxy-5-arsonopropiophenone were prepared by diazotization of the corresponding amino derivative followed by coupling with sodium arsenite. The same compounds were formed also by methylation of the product from the direct arsonation of 2,4-dihydroxyacetophenone and 2,4-dihydroxypropiophenone.

2. 2,4-Dihydroxypropiophenone was obtained by the nuclear condensation of propionitrile and resorcinol under the conditions of a Hoesch reaction.[6]

3. Several intermediate compounds and compounds incidental to the problem were prepared and identified for the first time.

4. All attempted arsonations of 2,4-dihydroxyacetophenone and 2,4-dihydroxypropiophenone by the Bart reaction[9] were unsuccessful.

LINCOLN, NEBRASKA RECEIVED JANUARY 20, 1937

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[15] The potentiometric method of Cislak and Hamilton [THIS JOURNAL, **52**, 638 (1930)] was used for the quantitative determination of arsenic in all arsenic-containing compounds prepared.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Influence of Cyclohexene Concentration in the Alkylation of Benzene by Cyclohexene. Dealkylation of Cyclohexylbenzenes

BY B. B. CORSON AND V. N. IPATIEFF

Direct alkylation of benzene with cycohexene, using aluminum chloride[1] or sulfuric acid[2] as catalyst, offers a convenient method for the preparation of cyclohexylbenzenes.

Bodroux employed a large excess of benzene and obtained monocyclohexylbenzene together with a small quantity of substance melting at 169–170° which had the carbon–hydrogen ratio of diphenylcyclohexane. He assumed that the latter resulted from the dehydrogenation and rearrangement of dicyclohexylbenzene. Truffault obtained monocyclohexylbenzene and 1,4-dicyclohexylbenzene.

This paper describes the effect of varying the amount of cyclohexene. Using aluminum chloride as catalyst, the following products were obtained: monocyclohexylbenzene, 1,4-dicyclohexylbenzene, 1,3,5-tricyclohexylbenzene and 1,2,3,5-tetracyclohexylbenzene. The tri and tetra derivatives are new. With sulfuric acid as catalyst, the products were: monocyclohexylbenzene, 1,4-dicyclohexylbenzene and 1,2,3,5-tetracyclohexylbenzene. The yields of the various products depend upon the relative proportions of benzene and cyclohexene, catalyst and conditions being constant.

Both catalysts gave some liquid product which analyzed for di derivative. Von Braun,[3] also, obtained liquid di derivative as by-product from the reaction between benzene and cyclohexylbromide. Although our product remained liquid at −77°, it still contained 1,4-dicyclohexylbenzene as shown by dehydrogenation.

Mono-, di- and tricyclohexylbenzenes can be alkylated to higher derivatives by cyclohexene. Both mono- and dicyclohexylbenzenes can be converted to tetra derivative. Tricyclohexylbenzene was not isolated. Tri derivative can be alkylated to tetra derivative, but the yield is small, the main product being liquid. Attempts to obtain penta- and hexacyclohexylbenzenes were unsuccessful.

Di-, tri- and tetracyclohexylbenzenes can be dealkylated to lower derivatives by the action of benzene in the presence of aluminum chloride. 1,4-Dicyclohexylbenzene and 1,3,5-tricyclohexylbenzene are converted to monocyclohexylbenzene. 1,2,3,5-Tetracyclohexylbenzene is dealkylated to monocyclohexylbenzene and 1,3,5-tricyclohexylbenzene. From the di, tri and tetra derivatives there was also obtained a small yield of material melting at 168–169° which had the carbon–hydrogen ratio of diphenylcyclohexane.[4]

The proof of structure of the mono derivative consisted in dehydrogenation by bromine to diphenyl. The di derivative was identical with 1,4-dicyclohexylbenzene prepared according to the method of von Braun,[3] who established its structure by dehydrogenation to 1,4-diphenylbenzene and by oxidation to terephthalic acid. Hydrogenation of the di derivative gave the two isomeric 1,4-dicyclohexylcyclohexanes described by von Braun.[5] The structure of the tri derivative was established by dehydrogenation to 1,3,5-triphenylbenzene and by hydrogenation to 1,3,5-tricyclohexylcyclohexane.[6]

The structure of the tetra derivative was based upon its easy dealkylation to 1,3,5-tricyclohexylbenzene and also upon its hydrogenation (accompanied by dealkylation) to 1,4-dicyclohexylcyclohexane and 1,3,5-tricyclohexylcyclohexane.[7]

Experimental

Benzene, Cyclohexene and Aluminum Chloride.—To a stirred, ice-cooled mixture of 176 g. (2.3 moles) of benzene and 60 g. of anhydrous aluminum chloride was added 246 g. (3 moles) of cyclohexene (b. p. 82–85°; d^{20}_{4}, 0.811; n^{20}_{D} 1.446). The time of addition was two and eight-tenths hours. The reaction temperature was 3–18°. After stirring an additional hour, the catalyst was decomposed with dilute acid and the mixture was filtered. Distillation and crystallization separated four cyclohexylbenzenes: 58 g. of monocyclohexylbenzene, 31 g. of 1,4-dicyclohexylbenzene, 158 g. of 1,3,5-tricyclohexylbenzene and 1 g. of 1,2,3,5-tetracyclohexylbenzene.

The constants of monocyclohexylbenzene are: b. p. 238.6–238.8° (756 mm.); m. p. 6.6–7.0°; d^{20}_{4} 0.944; n^{20}_{D} 1.5254.

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(1) Bodroux, *Ann. chim.*, [10] **11**, 511 (1928); see Berry and Reid, THIS JOURNAL, **49**, 3142 (1927).

(2) Truffault, *Compt. rend.*, **202**, 1286 (1936); the work described below was done before the appearance of Truffault's paper.

(3) Von Braun, *Ber.*, **60**, 1180 (1927).

(4) The reaction responsible for this product will be discussed in a later paper.

(5) Von Braun, Irmisch and Nelles, *Ber.*, **66**, 1471 (1933).

(6) Adkins, Zartman and Cramer, THIS JOURNAL, **53**, 1425 (1931).

(7) Tetraphenylmethane also dealkylates during hydrogenation; Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, 1936, p. 239.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.9; H, 10.1; mol. wt., 160. Found: C, 90.2; H, 9.9; mol. wt., 158.

1,4-Dicyclohexylbenzene (m. p. 102–103°) was found in the mother liquor from the crystallization of the tri derivative.

Anal. Calcd. for $C_{18}H_{26}$: C, 89.2; H, 10.8; mol. wt., 242. Found: C, 89.1; H, 10.8; mol. wt., 241.

Six cc. of oil was obtained which also had the carbon-hydrogen ratio of dicyclohexylbenzene. Its constants were: b. p. 335–340° (756 mm.); d^{20}_4 0.966; n^{20}_D 1.5357; C, 88.8; H, 10.9; mol. wt., 242. Dehydrogenation with bromine gave some 1,4-diphenylbenzene, showing that the original liquid contained 1,4-dicyclohexylbenzene.

1,3,5-Tricyclohexylbenzene melts at 68.5–69° after crystallizing from acetone. The air-dried material melts low, but after warming in a vacuum the melting point is sharp. It is very soluble in benzene, cyclohexane, carbon tetrachloride, and chloroform; less soluble in acetone, dioxane, and the lower alcohols.

Anal. Calcd. for $C_{24}H_{36}$: C, 88.8; H, 11.2; mol. wt., 324. Found: C, 88.5; H, 11.2; mol. wt., 350.

1,2,3,5-Tetracyclohexylbenzene melts at 264–265° after crystallizing from benzene. It is soluble in benzene, cyclohexane, carbon tetrachloride and chloroform; less soluble in acetic acid, acetone, ether and the lower alcohols.

Anal. Calcd. for $C_{30}H_{46}$: C, 88.6; H, 11.4; mol. wt., 406. Found: C, 88.3; H, 11.4; mol. wt., 414.

A fair yield of tetra derivative was obtained by increasing the ratio of cyclohexene to benzene, and using cyclohexane as solvent. In the absence of solvent, the mixture became too thick for effective stirring. To a mixture of 156 g. (2 moles) of benzene, 60 g. of aluminum chloride and 150 g. of cyclohexane was added 328 g. (4 moles) of cyclohexene. The time of addition was three and one-half hours. The reaction temperature was 3–20°. The products were: 20 g. of monocyclohexylbenzene, 35 g. of 1,4-dicyclohexylbenzene, 150 g. of 1,3,5-tricyclohexylbenzene and 80 g. of 1,2,3,5-tetracyclohexylbenzene.

Benzene, Cyclohexene and Sulfuric Acid.—Monocyclohexylbenzene was obtained as main product when 164 g. (2 moles) of cyclohexene was added to a stirred, ice-cooled mixture of 408 g. (6 moles) of benzene and 92 g. of 96% sulfuric acid. The time of addition was two hours. The hydrocarbon layer was washed with two 50-cc. portions of cold 96% sulfuric acid,[8] followed by water, 3% caustic, and water. The dried hydrocarbon was twice distilled through a short column. The yield of monocyclohexylbenzene was 200 g. (b. p. 239–245° at 760 mm.). The hydrocarbon fractions boiling at 78–83°, 83–235°, 235–239°, 245–265°, 265–300° and above 300° weighed 320, 2, 2, 11, 4 and 63 g., respectively.

The filtrate from the semi-solid bottoms was freed from unsaturates by shaking with cold 96% sulfuric acid, followed by distillation. The distillate did not solidify at −77°. Its constants were similar to those of the liquid mixture of isomeric dicyclohexylbenzenes obtained with aluminum chloride as catalyst (b. p. 332–335° at 742 mm.; d^{20}_4 0.969; n^{20}_D 1.5366; C, 88.8; H, 10.9; mol. wt., 253).

A satisfactory yield of 1,4-dicyclohexylbenzene could not be obtained by increasing the cyclohexene–benzene ratio.

A reaction mixture of 164 g. (2 moles) of cyclohexene, 156 g. (2 moles) of benzene, and 92 g. of sulfuric acid gave mono derivative as main product, 143 g. Fifty-one grams of crude solid was filtered from the bottoms (90 g.). Crystallization of the solid gave 26 g. of pure di compound and 11 g. of impure material melting at 95–99°.

Starting with 246 g. (3 moles) of cyclohexene, 156 g. (2 moles) of benzene, and 92 g. of sulfuric acid gave 95 g. of crude monocyclohexylbenzene and 170 g. of bottoms distilling above 300°. The latter deposited solid on standing. Filtration gave 94 g. of solid and 69 g. of oil. Seventy-one grams of pure 1,4-dicyclohexylbenzene was obtained by recrystallizing the crude solid.

When the cyclohexene–benzene ratio was greater than 1.5, there was excessive tar formation. An experiment was made with 328 g. (4 moles) of cyclohexene, 156 g. (2 moles) of benzene, and 92 g. of sulfuric acid. The reaction mixture was so dark that it was difficult to separate the acid layer. Troublesome emulsions were encountered when the hydrocarbon layer was washed. Seventy-five grams of monocyclohexylbenzene and 199 g. of bottoms (above 300°) were obtained. From the latter was obtained 61 g. of 1,4-dicyclohexylbenzene and 1.5 g. of 1,2,3,5-tetracyclohexylbenzene. The filtrate (110 g.) was not investigated.

Alkylation of Mono-, Di- and Tricyclohexylbenzenes.—Ninety-eight grams (1.2 moles) of cyclohexene was added during one hour to a mixture of 160 g. (1 mole) of monocyclohexylbenzene, 80 g. of cyclohexane, and 92 g. of 96% sulfuric acid. The reaction temperature was 2–14°. The following compounds were isolated: 70 g. of monocyclohexylbenzene, 23 g. of 1,4-dicyclohexylbenzene and 12 g. of 1,2,3,5-tetracyclohexylbenzene. The greater part of the tetra derivative separated from the catalyst acid on standing.

Forty-one grams (0.5 mole) of cyclohexene was added to a mixture of 58 g. (0.24 mole) of 1,4-dicyclohexylbenzene, 80 g. of cyclohexane and 20 g. of anhydrous aluminum chloride. The time of addition was one hour. The reaction temperature was 3–7°. Forty-nine grams of 1,4-dicyclohexylbenzene and 16 g. of 1,2,3,5-tetracyclohexylbenzene were isolated. When the reaction was run at 80°, the products were 35 g. of 1,4-dicyclohexylbenzene and 9 g. of 1,2,3,5-tetracyclohexylbenzene, plus 25 g. of liquid boiling from 300 to 425°.

Twelve and three-tenths grams (0.15 mole) of cyclohexene was added to a mixture of 32.4 g. (0.1 mole) of 1,3,5-tricyclohexylbenzene, 80 g. of cyclohexane, and 20 g. of aluminum chloride. The time of addition was one hour. Different reaction temperatures were tried; 11–15°, 34–37° and 80–83°. The solid products isolated from these experiments were: 19 g. of tri and 1 g. of tetra derivative; 15 g. of tri and 0.3 g. of tetra derivative; 7.7 g. of tri derivative, respectively.

Dealkylation of Di-, Tri- and Tetracyclohexylbenzenes.—1,4-Dicyclohexylbenzene (24.2 g.; 0.1 mole) was stirred for two hours at 80–83° with 195 g. (2.5 moles) of benzene and 20 g. of aluminum chloride. Eighteen grams of monocyclohexylbenzene was obtained; also 5 g. of liquid which distilled at 330–350°, and 6 g. of bottoms. Both of the

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[8] The purpose of the sulfuric acid was to remove esters which would otherwise decompose to tar during distillation; see Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936).

latter fractions deposited crystals which melted at 168–169° after crystallizing from acetone.

1,3,5-Tricyclohexylbenzene (32.4 g., 0.1 mole) was stirred for two hours at different temperatures with 195 g. (2.5 moles) of benzene and 20 g. of aluminum chloride. Depending on the temperature, the main product was monocyclohexylbenzene or unchanged tri derivative. At 22–27° the products were 4.2 g. of mono derivative and 20.8 g. of tri derivative; at 50–55°, 23 g. of mono derivative; at 80–83°, 15 g. of mono derivative. The amount of viscous bottoms increased with the temperature. There was also a small fraction boiling at 330–350° which deposited solid on standing which melted at 168–169° and which was identical with the solid obtained from the di derivative. With anhydrous ferric chloride as catalyst, neither monocyclohexylbenzene nor the 330–350° fraction was obtained. The viscous bottoms were not investigated.

1,2,3,5-Tetracyclohexylbenzene (40.6 g., 0.1 mole) was stirred at 20–23° for two and one-half hours with 98 g. (1.25 moles) of benzene and 20 g. of aluminum chloride. Eleven grams of monocyclohexylbenzene (b. p. 235–241°; n^{20}_D 1.525) and 20 g. of 1,3,5-tricyclohexylbenzene were isolated. The identity of the mono derivative was established by dehydrogenation to diphenyl (m. p. 68–69°; mixed m. p. 69–70.5°). The tri derivative melted at 67–68° and showed no depression when melted with an equal quantity of 1,3,5-tricyclohexylbenzene. A fraction boiling at 330–350° was also obtained. This liquid deposited solid melting at 168–169°, which was identical with that obtained in the dealkylation of 1,4- and 1,3,5-tricyclohexylbenzenes.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.2; H, 8.6.

Repetition of this experiment at 80°, using 40.6 g. (0.1 mole) of tetra compound, 195 g. (2.5 moles) of benzene, and 20 g. of aluminum chloride gave 25 g. of monocyclohexylbenzene and 4 g. of material boiling at 300–350°. The latter deposited crystals of the 168–169° compound.

Proof of Structure.—Monocyclohexylbenzene was dehydrogenated to diphenyl. Forty-eight grams of bromine was added during two hours to 16 g. of monocyclohexylbenzene at 165°. The bromine was consumed quickly and hydrogen bromide was evolved. The product distilled at 253–273° (755 mm.) and the distillate solidified. The recrystallized solid melted at 68–69° (yield 14 g.). The mixed melting point with diphenyl was 69–70.5°.

Dicyclohexylbenzene was identical by mixed melting point with 1,4-dicyclohexylbenzene prepared according to the method of von Braun,[3] from cyclohexyl bromide, benzene and aluminum chloride.

Hydrogenation of dicyclohexylbenzene gave two isomeric dicyclohexylcyclohexanes. Forty-eight grams of di derivative (dissolved in 100 cc. of cyclohexane) was heated fourteen hours at 220° with 5 g. of nickel catalyst and an initial hydrogen pressure of 100 kg./sq. cm. The main product was the isomer melting at 159.5–161° (calcd.: C, 87.0; H, 13.0. Found: C, 86.9; H, 13.0). The other isomer melted at 54–56° (Found: C, 86.9; H, 13.0.)

Tricyclohexylbenzene was dehydrogenated to 1,3,5-triphenylbenzene. Thirty-six grams of bromine was added to 8 g. of tricyclohexylbenzene at 165°. Hydrogen bromide was evolved. The reaction product was distilled at 4 mm., 7 g. boiling at 230–250°. The distillate solidified. It was crystallized from absolute alcohol; m. p. 168–170°. Combustion gave low figures for carbon (calcd.: C, 94.07; H, 5.93. Found: C, 92.68, 92.74; H, 5.97, 5.98). A 50–50 mixture of 1,3,5-triphenylbenzene (m. p. 171–172°)[9] and dehydrogenation product melted at 170–171°.

Hydrogenation of the tri derivative gave tricyclohexylcyclohexane; m. p. 158–159° after crystallizing from cyclohexane–acetone. Thirty grams of tricyclohexylbenzene (dissolved in 100 cc. of cyclohexane) was heated for twenty hours at 240° with 5 g. of nickel catalyst and an initial hydrogen pressure of 120 kg./sq. cm.

Anal. Calcd. for $C_{24}H_{42}$: C, 87.2; H, 12.8. Found: C, 86.9; H, 12.9.

Tetracyclohexylbenzene was assumed to be the 1,2,3,5-derivative because of its easy dealkylation to 1,3,5-tricyclohexylbenzene.

Hydrogenation of the tetra derivative gave mainly 1,3,5-tricyclohexylcyclohexane, together with a smaller amount of 1,4-dicyclohexylcyclohexane. Fifty-one grams of tetracyclohexylbenzene (dissolved in 100 cc. of cyclohexane) was heated for twelve hours at 250° and twelve hours at 280° with 5 g. of nickel catalyst and an initial hydrogen pressure of 100 kg./sq. cm. A small amount of liquid product, obtained from the mother liquor, was not investigated.

Acknowledgment.—The authors express their thanks to Mr. Wilbur Shand for assistance in the experimental work and to Mr. Reno Moehl for carbon–hydrogen analyses.

Summary

Benzene reacts with cyclohexene to form mono-, di-, tri- and tetracyclohexylbenzenes. The nature of the product depends upon the relative amount of cyclohexene. The reaction is catalyzed by aluminum chloride and also by sulfuric acid.

Mono-, di- and tricyclohexylbenzenes react with cyclohexene to form higher derivatives.

Di-, tri- and tetracyclohexylbenzenes react with benzene, in the presence of aluminum chloride, to form lower derivatives.

Di- and tricyclohexylbenzenes are hydrogenated to di- and tricyclohexylcyclohexanes, respectively. Tetracyclohexylbenzene is dealkylated during hydrogenation, the products being di- and tricyclohexylcyclohexanes.

RIVERSIDE, ILLINOIS RECEIVED JANUARY 18, 1937

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[9] Dolgov and Volnov, *J. Gen. Chem.* (U. S. S. R.), **1**, 340 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Ternary Systems Barium Hydroxide and Water with Barium Chloride, Thiocyanate, Chlorate or Acetate at 25°

BY H. W. FOOTE AND F. C. HICKEY, O.P.

It has been shown by phase-rule methods that barium forms a basic chloride,[1] bromide and iodide[2]; and that it forms no basic nitrate.[3] The conditions for the formation of the so-called basic salt $BaOH{\cdot}SH{\cdot}5H_2O$ have been determined by Terres and Brückner[4] but there appears to be no reason why this compound may not be more simply considered as $BaS{\cdot}6H_2O$, a compound which has been known for many years. In fact, the work of these investigators shows that no basic barium sulfide exists over a wide range of temperature. Except for these cases, no systematic attempts have been made to determine to what extent barium forms basic salts. On account of the considerable solubility of the hydroxide, however, basic barium salts, if they form, can readily be determined by isothermal solubility diagrams. The results obtained on four systems at 25° are given in the present paper.

Materials and Methods

Barium hydroxide, chlorate and chloride were recrystallized before use, the first in a special apparatus which excluded carbon dioxide. We were fortunate in having samples of the thiocyanate and acetate of excellent purity which were used without further purification.[5]

Barium hydroxide was determined by titration with standard hydrochloric acid, using nitrazine yellow as indicator in the presence of the chloride, thiocyanate and chlorate; and phenolphthalein in the presence of the acetate. The acid was standardized by titrating barium hydroxide solutions whose concentration was determined by converting the hydroxide to the chloride, evaporating and drying to constant weight. This standard agreed closely with that obtained by determining the chloride gravimetrically as silver chloride. In the systems containing chloride, chlorate or acetate, total barium was determined by evaporating with hydrochloric acid, and weighing barium chloride. In the system containing thiocyanate, this radical was determined directly by the usual method with standard silver nitrate, using ferric alum as indicator.

Mixtures of the three components in suitable proportions were rotated in the thermostat at 25° for several days. In no case was difficulty experienced in obtaining equilibrium in two days. The temperature variation of the thermostat was not greater than ±0.03° which affects the results less than can be detected by analysis. Samples of solution for analysis were drawn off through asbestos or glass wool filters, or, when the solid settled properly, without filtering, and weighed. When barium hydroxide alone or a single barium salt was present in the residue, it was in most cases not analyzed as qualitative tests were sufficient to identify it. When an analysis was necessary, the residues were removed and dried almost completely between filter papers as rapidly as possible. This material, as it contained a small amount of residual solution, involved the use of the well-known Schreinemakers method for deriving the composition of the residues free of solution. By drying the residues almost completely only a short extrapolation of the results is necessary, which is of importance in the case of hydrated compounds for the accurate determination of the amount of water. On the other hand, the hydroxide, during exposure to the air, becomes slightly carbonated, which in the analysis, gives a somewhat low result for the hydroxide and a correspondingly high result for the salt present. The error from this source, however, is less important than the error from a long extrapolation as there is no difficulty in determining the ratio of the hydroxide to the salt with sufficient accuracy, and the chief difficulty is in determining the water of hydration. From the nature of the case, the composition of the solutions can be determined more accurately than the composition of the residues.

System: $Ba(OH_2)$–$BaCl_2$–H_2O.—This system has been investigated at 30° by Schreinemakers,[1] who found the basic salt $BaOHCl{\cdot}2H_2O$. We have determined the solubility curve at 25° to make the results comparable with the other systems, all of which have been determined at this temperature. The data for the curves where barium chloride or barium hydroxide alone were the solid phases were obtained with considerably more care and are more numerous than was perhaps necessary for the system, as the results were needed in connection with another investigation. These determinations were made in duplicate and the titration of the hydroxide was carried out with a weight buret.

The solubility results are given in Table I. Only enough wet residues were analyzed to confirm the formula of Schreinemakers,[1] $BaOHCl{\cdot}2H_2O$. All data represent percentages by weight.

The solubility data are plotted in Fig. 1 together with the composition of the three wet residues analyzed, which were in equilibrium with pure double salt. Results at univariant points were averaged. To avoid confusion, the data have been omitted along the short curve where barium chloride was the solid phase.

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[1] Schreinemakers, *Z. physik. Chem.*, **68**, 83 (1910).

[2] Milikan, *ibid.*, **92**, 59, 496 (1918).

[3] Parsons and Carson, THIS JOURNAL, **32**, 1383 (1910).

[4] Terres and Brückner, *Z. Elektrochem.*, **26**, 1 (1920).

[5] Barium thiocyanate crystallizes at room temperatures as the compound $Ba(CNS)_2{\cdot}3H_2O$. It was originally described incorrectly as the dihydrate and this error has been retained in many references to the compound. Whether a dihydrate is formed at a higher temperature has not been determined.

TABLE I

SYSTEM: $Ba(OH)_2$–$BaCl_2$–H_2O AT 25°

Solution % $Ba(OH)_2$	Solution % $BaCl_2$	Wet residue % $Ba(OH)_2$	Wet residue % $BaCl_2$	Residue contains:
4.489	None	..	..	$Ba(OH)_2·8H_2O$
4.224	3.649	..	..	$Ba(OH)_2·8H_2O$
4.100	6.788	..	..	$Ba(OH)_2·8H_2O$
4.04	10.10	..	..	$Ba(OH)_2·8H_2O$
4.03	12.62	..	..	$Ba(OH)_2·8H_2O$
4.05	15.33	..	..	$Ba(OH)_2·8H_2O$
4.06	17.05	..	..	$Ba(OH)_2·8H_2O$
4.11	19.31	..	..	$Ba(OH)_2·8H_2O$ $BaOHCl·2H_2O$
4.13	19.32	..	..	$Ba(OH)_2·8H_2O$ $BaOHCl·2H_2O$
3.38	20.79	35.3	45.5	$BaOHCl·2H_2O$
3.13	22.05	34.0	44.9	$BaOHCl·2H_2O$
2.65	23.57	35.1	46.9	$BaOHCl·2H_2O$
1.94	26.69	..	..	$BaOHCl·2H_2O$ $BaCl_2·2H_2O$
1.95	26.71	..	..	$BaOHCl·2H_2O$ $BaCl_2·2H_2O$
1.77	26.72	..	..	$BaCl_2·2H_2O$
1.39	26.83	..	..	$BaCl_2·2H_2O$
0.89	26.94	..	..	$BaCl_2·2H_2O$
None	27.16	..	..	$BaCl_2·2H_2O$

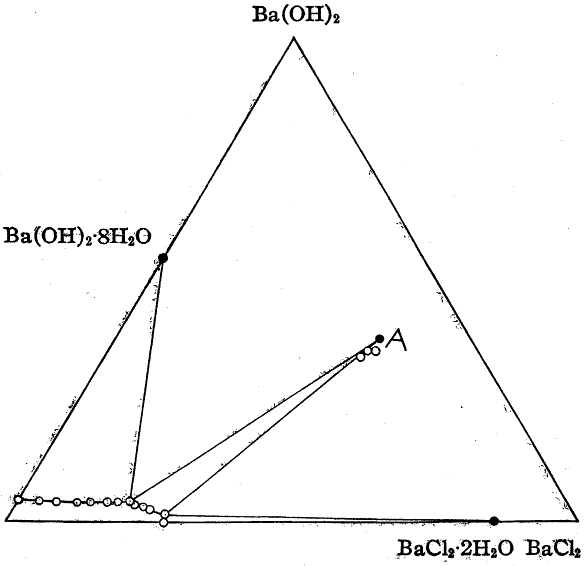

Fig. 1.—System $Ba(OH)_2$–$BaCl_2$–H_2O. Solid phases are $Ba(OH)_2·8H_2O$, $BaCl_2·2H_2O$ and $BaOHCl·2H_2O$ (A in diagram).

System: $Ba(OH)_2$–$Ba(CNS)_2$–H_2O.—The results are given in Table II.

TABLE II

SYSTEM: $Ba(OH)_2$–$Ba(CNS)_2$–H_2O AT 25°

Solution % $Ba(OH)_2$	Solution % $Ba(CNS)_2$	Wet residue % $Ba(OH)_2$	Wet residue % $Ba(CNS)_2$	Residue contains:
4.489	None	..	..	$Ba(OH)_2·8H_2O$
3.58	15.83	..	..	$Ba(OH)_2·8H_2O$
3.44	26.54	..	..	$Ba(OH)_2·8H_2O$
5.89	47.51	52.4	2.4	$Ba(OH)_2·8H_2O$
8.45	50.88	44.2	24.3	$Ba(OH)_2·8H_2O$ BaOHCNS
8.49	51.00	35.7	50.5	$Ba(OH)_2·8H_2O$ BaOHCNS
6.16	54.49	34.7	59.7	BaOHCNS
4.75	57.34	37.7	59.0	BaOHCNS
3.18	61.61	31.8	59.9	BaOHCNS $Ba(CNS)_2·3H_2O$
3.16	61.73	1.4	80.9	BaOHCNS $Ba(CNS)_2·3H_2O$
2.05	61.97	0.1	81.7	$Ba(CNS)_2·3H_2O$
None	62.63	..	..	$Ba(CNS)_2·3H_2O$

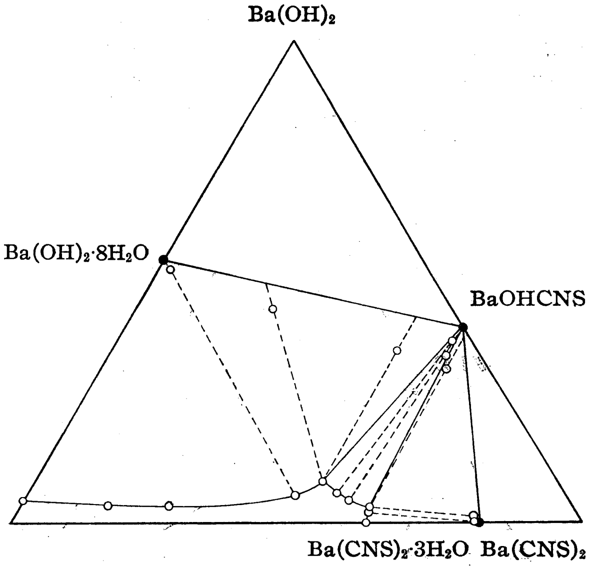

Fig. 2.—System $Ba(OH)_2$–$Ba(CNS)_2$–H_2O. Solid phases are $Ba(OH)_2·8H_2O$, $Ba(CNS)_2·3H_2O$ and BaOHCNS.

The results in Table II are plotted in Fig. 2. Tie lines connecting solutions and residues are shown as dotted lines. The solid in one of the wet residues at the univariant point where basic salt and thiocyanate are in equilibrium was nearly pure basic salt and the point representing the composition of the residue has been shifted slightly to the right for clarity.

It was difficult to obtain the basic salt in pure condition as the crystals were very small and only formed in solutions containing a large excess of thiocyanate. A sample of the salt for analysis was prepared by crystallizing a small amount at 25° from a solution of the proper concentration. This material gave on analysis

$Ba(OH)_2$, 38.53; $Ba(CNS)_2$, 59.16; H_2O (diff.), 2.31

corresponding to the molecular ratio 1:1.04:0.57. As the material could not be dried properly, the water is undoubtedly from the solution and the result confirms the formula mentioned above.

System: $Ba(OH)_2$–$Ba(ClO_3)_2$–H_2O.—This system forms no basic salt at 25° and the only solids occurring are hydrated barium hydroxide and barium chlorate, which crystallizes as the anhydrous salt. The solubility results are given in Table III. They are plotted in Fig. 3 together with the composition of the only two wet residues which it was necessary to analyze.

Table III

System: $Ba(OH)_2$–$Ba(ClO_3)_2$–H_2O at 25°

Solution		Wet residue		
% $Ba(OH)_2$	% $Ba(ClO_3)_2$	% $Ba(OH)_2$	% $Ba(ClO_3)_2$	Residue contains:
4.489	None	..	..	$Ba(OH)_2 \cdot 8H_2O$
4.02	8.79	..	..	$Ba(OH)_2 \cdot 8H_2O$
3.85	15.98	..	..	$Ba(OH)_2 \cdot 8H_2O$
3.77	21.85	..	..	$Ba(OH)_2 \cdot 8H_2O$
3.72	26.55	51.4	3.2	$Ba(OH)_2 \cdot 8H_2O$ $Ba(ClO_3)_2$
3.71	26.62	3.6	81.6	$Ba(OH)_2 \cdot 8H_2O$ $Ba(ClO_3)_2$
1.87	27.17	..	..	$Ba(ClO_3)_2$
None	27.58	..	..	$Ba(ClO_3)_2$

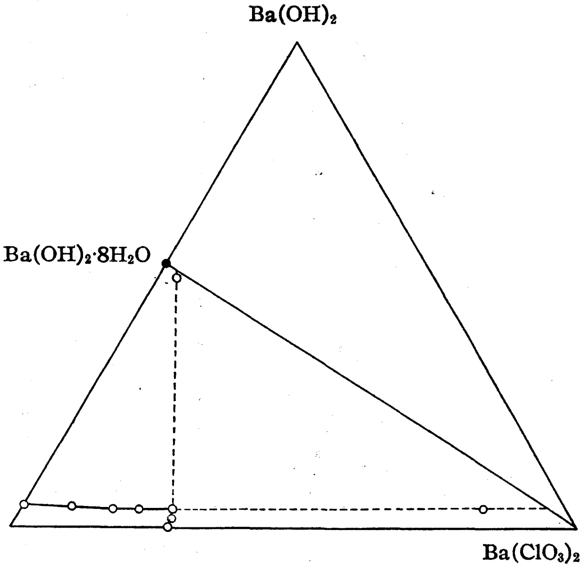

Fig. 3.—System $Ba(OH)_2$–$Ba(ClO_3)_2$–H_2O. Solid phases are $Ba(OH)_2 \cdot 8H_2O$ and $Ba(ClO_3)_2$.

System: $Ba(OH)_2$–$Ba(C_2H_3O_2)_2$–H_2O.—This system, like the previous one, forms no basic salt. At 25° the monohydrate is the stable form of barium acetate in contact with solutions. The results are given in Table IV and plotted in Fig. 4.

Table IV

System: $Ba(OH)_2$–$Ba(C_2H_3O_2)_2$–H_2O at 25°

Solution		Wet residue		
% $Ba(OH)_2$	% $Ba(C_2H_3O_2)_2$	% $Ba(OH)_2$	% $Ba(C_2H_3O_2)_2$	Residue contains:
4.489	None	...	...	$Ba(OH)_2 \cdot 8H_2O$
3.22	16.91	52.74	1.14	$Ba(OH)_2 \cdot 8H_2O$
2.85	29.32	51.80	2.45	$Ba(OH)_2 \cdot 8H_2O$
2.64	37.97	50.31	4.73	$Ba(OH)_2 \cdot 8H_2O$
2.56	41.71	39.86	23.42	$Ba(OH)_2 \cdot 8H_2O$ $Ba(C_2H_3O_2)_2 \cdot H_2O$
2.56	41.71	27.53	43.45	$Ba(OH)_2 \cdot 8H_2O$ $Ba(C_2H_3O_2)_2 \cdot H_2O$
2.60	41.80	3.81	83.91	$Ba(OH)_2 \cdot 8H_2O$ $Ba(C_2H_3O_2)_2 \cdot H_2O$
1.35	42.40	Trace	93.71	$Ba(C_2H_3O_2O_2 \cdot H_2O$
None	43.20	None	91.72	$Ba(C_2H_3O_2)_2 \cdot H_2O$

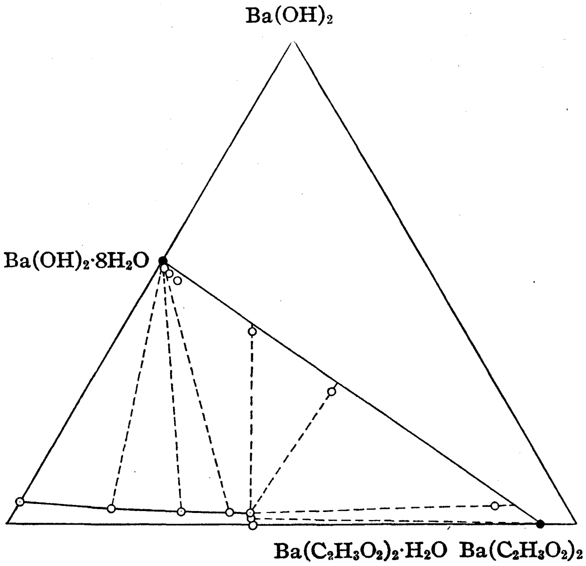

Fig. 4.—System $Ba(OH)_2$–$Ba(C_2H_3O_2)_2$–H_2O. Solid phases are $Ba(OH)_2 \cdot 8H_2O$ and $Ba(C_2H_3O_2)_2 \cdot H_2O$.

Summary

Isothermal solubility determinations (at 25°) have been made in the ternary systems composed of barium hydroxide and water with barium chloride, thiocyanate, chlorate or acetate. The basic salt $BaOHCl \cdot 2H_2O$, investigated by Schreinemakers at another temperature, has been found. A new basic salt BaOHCNS also has been found. No basic chlorate or acetate forms at this temperature, the solid phases being the same that crystallize in the binary systems with water alone.

New Haven, Conn. Received January 18, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 59]

Fluorochlorobromides of Silicon

BY WALTER C. SCHUMB AND HERBERT H. ANDERSON

By the use of methods previously employed successfully in the preparation of mixed halides of silicon, such as the fluorochlorides, fluorobromides, and chlorobromides, we have prepared for the first time halides of silicon containing three different halogens, namely, $SiFClBr_2$ and $SiFCl_2Br$.[1] In the course of this work new methods of preparation of the silicon chlorobromides also have been developed.

In a previous paper[2] we have described the reaction of silicon tetrabromide with antimony trifluoride, in the absence of any catalyst, by which a mixture of fluorobromides of silicon was obtained. It seemed wholly reasonable, therefore, to expect that the partial fluorination of a chlorobromide, such as $SiClBr_3$ or $SiCl_2Br_2$, should yield products containing three different halogens. The following experimental work bears out the correctness of this assumption.

A. Reactions of Antimony Trifluoride with Silicon Chlorobromides

The silicon chlorobromides needed for these experiments were prepared by the following methods, of which all but the first have not been described previously.

1. A mixture of chlorine and bromine was passed over metallic silicon at 700°, and the products were subjected to repeated distillation. In this way silicon chlorotribromide (b. p. 126–130°) and silicon dichlorodibromide (b. p. 102–106°) were obtained, together with some trichlorobromide and tetrabromide.

2. A mixture of the three chlorobromides of silicon was also prepared by refluxing silicon tetrabromide for forty-eight hours in an atmosphere of chlorine, contained in a sealed liter bulb, a microburner supplying the heat and the upper portion of the flask serving as a condensing surface. The mixture was separated by fractional distillation.

3. It was found that the reaction of antimony trichloride, mixed in the proper proportions with silicon tetrabromide, and subjected to the proper mode of distillation, may also serve as a convenient method for preparing any one of the three chlorobromides, $SiCl_3Br$, $SiCl_2Br_2$ or $SiClBr_3$, in yields of approximately 80%.[3]

4. A liquid mixture of bromine and hexachlorodisilane, Si_2Cl_6, was dropped from a separatory funnel into a horizontal Pyrex tube maintained at 500° in a gas furnace. A slow stream of pure carbon dioxide passing through the tube carried the products of the reaction to condensers, cooled by ice, and thence to a drying tube. As the mixture of liquids entered the heated tube vaporization occurred, followed immediately by reaction accompanied by flame. The free bromine left in the reaction products was removed quantitatively by shaking with mercury. From an original 100 g. of Si_2Cl_6 and 65 g. of bromine which was actually used in the reaction, about 40 g. was obtained of each of the three substances, silicon tetrachloride, trichlorobromide and dichlorodibromide.

In a similar manner, 90 g. of octachlorotrisilane, Si_3Cl_8, with 44 g. of bromine (1:1.1 mol.) gave as final, colorless products:

	B. p., °C.	Grams
$SiCl_4$	57	20
$SiCl_3Br$	80	30
$SiCl_2Br_2$	105	18
$SiClBr_3$	128	8
Si_2Cl_6	147	6

A small, higher boiling residue was also obtained

During a period of one hour 230 g. of sublimed antimony trifluoride was added gradually with rapid stirring to 900 g. of silicon chlorotribromide, $SiClBr_3$, contained in a three-necked flask, which was provided with a mercury-sealed stirrer and connected to a series of condensing traps provided with circular coils. Distillation of the product formed in the first condenser, maintained at 0°, yielded about 75 g. of silicon fluorochlorodibromide, $SiFClBr_2$, b. p. 59.5°; and from the second condenser, maintained at −65°, about 20 cc. of a liquid was obtained which contained no bromine and proved to be a mixture of the fluorochlorides, SiF_2Cl_2 and SiF_3Cl, in molar proportions approximately 2:1.

The fact that a dichloro compound is formed from a monochloro compound in this process may be explained when it is realized that antimony trichloride, formed in the interaction of SbF_3 and $SiClBr_3$, is capable of bringing about replacement of bromine atoms by chlorine in such compounds as silicon tetrabromide, as stated above. Consequently, in the reaction of antimony trifluoride with silicon chlorotribromide the formation of a dichloro compound is to be interpreted as due to side reactions in which both antimony trifluoride and antimony trichloride are involved in interaction with $SiClBr_3$.

In a similar manner, 130 g. of antimony trifluoride was added to 400 g. of silicon dichlorodibromide, $SiCl_2Br_2$, over a period of eighty minutes, the condensers being cooled with ice and with a mixture of carbon dioxide and alcohol, respectively. The contents of the first receiver

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(1) The third possible compound containing the same elements, SiF_2ClBr, has not as yet been isolated, although several methods for its preparation have been tried.

(2) Schumb and Anderson, THIS JOURNAL, **58**, 994 (1936).

(3) From a mixture of equal weights of $SiBr_4$ and PCl_5 heated for one hour, a mixture of $SiClBr_3$ and $SiCl_2Br_2$ was also obtained.

consisted of 40 g. of a liquid boiling at about 39°. Repeated distillation of this mixture finally yielded 10 g. of pure $SiFCl_2Br$, b. p. 35.1 ± 0.2° at 752 mm. (corr.). The analyses of the new compounds, as well as determinations of their molecular weights and vapor pressures, are given below (section D).

B. Chlorination of Silicon Fluorobromides

Silicon fluorotribromide and chlorine were mixed in a liter globe in the molar ratio $4SiFBr_3:3Cl_2$, the initial pressure of chlorine being two atmospheres. Although reaction began upon standing at room temperature, the globe was gently heated at the bottom with a very small flame for two hours; at the end of this period the reaction was complete. Mercury was then introduced into the cooled globe and the free bromine quantitatively removed thereby. Distillation of the product yielded a mixture of nearly equal weights of $SiFClBr_2$ and $SiFCl_2Br$, together with some $SiFCl_3$, and a residue containing a small quantity of unchanged $SiFBr_3$. The chief reaction may be represented as

$$4SiFBr_3 + 3Cl_2 \longrightarrow 2SiFClBr_2 + 2SiFCl_2Br + 3Br_2$$

The reaction between gaseous silicon difluorodibromide and chlorine proceeded very slowly at temperatures below 400°. Radiation with a 500-watt lamp for several hours did not noticeably increase the rate of reaction. When a mixture of SiF_2Br_2 and chlorine in the molar ratio of 3:2 was passed repeatedly through a 20-mm. Pyrex tube, 80 cm. long, placed in a furnace at 500°, the reaction was sufficiently rapid for study. Bromine was liberated copiously, and its removal from the products was effected by shaking with an excess of mercury. The resulting gas mixture, after being transferred to the usual fractionating system, gave a fraction which proved to be substantially pure silicon difluorodichloride (v. p. 59 mm. at −78°) and a small residue consisting mainly of silicon difluorodibromide. Hence the original reaction taking place proceeded essentially as follows

$$SiF_2Br_2 + Cl_2 = SiF_2Cl_2 + Br_2$$

and no fluorochlorobromides were formed in this case.

C. Reaction of Antimony Trichloride with $SiFBr_3$

In view of the fact, referred to in section A, that antimony trichloride brings about the replacement of bromine by chlorine in silicon tetrabromide, it was felt that interaction of antimony trichloride and $SiFBr_3$ might yield fluorochlorobromides. In one experiment 50 g. of the fluorotribromide was added to 30 g. of anhydrous antimony trichloride in a 50-cc. flask, provided with a 15-cm. fractionating column (8 mm. o. d.) containing within it a glass rod and aluminum spiral. The mixture was heated cautiously with a microburner and a distillate passed over at 58–64°, the products consisting of $SiFCl_2Br$, $SiFClBr_2$ and unchanged $SiFBr_3$, in the approximate ratio of 2:1:1. The fluorochlorodibromide was purified by distillation, and its boiling point was determined as 59.5 ± 0.2° at 760 mm. It was quite free from silicon tetrachloride (b. p. 56.8°).

In another experiment a water-jacketed fractionating column (45 cm. long and 6 mm. o. d., without spiral) was used, the temperature of the jacket being kept at 35°. In this experiment a mixture of 50 g. of $SiFBr_3$ and 43 g. of $SbCl_3$ was warmed very cautiously in the 50-cc. flask for one hour, the antimony trichloride remaining solid. The original distillate, weighing 32 g., in this case passed over between 34–38°, and consisted of $SiFCl_2Br$, $SiFCl_3$ and $SiFClBr_2$ in the approximate ratio 8:3:1.

D. Analysis and Properties of Silicon Fluorochlorobromides

In the analysis of the two fluorochlorobromides the sample, contained in a small weighed bulb, supplied with a cap consisting of a 20 mm. ground joint and stopcock, was hydrolyzed by ice-cold water, which was caused to enter the bulb by opening the stopcock under the water, the bulb being cooled. The products of hydrolysis are silicic, hydrochloric, hydrobromic and hydrofluoric acids. If the temperature is low and the concentration of hydrofluoric acid is small, very little fluosilicic acid is formed.

The analysis itself consisted of weighing the silica; of liberating bromine by means of cold 10% potassium permanganate solution and nitric acid, and after extraction of the bromine with carbon tetrachloride, determining it iodimetrically; and of determining the chlorine in solution as silver chloride after treatment with nitrous acid. Direct determination of fluorine was made in the case of $SiFClBr_2$, by hydrolyzing the sample, and after the filtration of the silica, which was washed with hot water, the filtrate was made alkaline and heated to 90° to convert any fluosilicate into fluoride. The filtered solution was acidified with acetic acid in the correct excess, and an excess of a solution of calcium chloride was added. After standing for two weeks, the precipitated calcium fluoride was filtered, washed, ignited and weighed. A summary of the analytical results is given in Table I.

The molecular weights, determined by the gas density method, as described in our previous paper (1), are also shown in the table.

TABLE I

ANALYTICAL RESULTS AND MOLECULAR WEIGHTS

Substance	Si, %	F, %	Cl, %	Br, %	Mol. wt.
$SiFClBr_2$	11.87	..	14.78	66.13	246.8
	10.97	7.78	14.57	65.81	245.8
Calcd.	11.58	7.84	14.63	65.94	242.3
$SiFCl_2Br$	13.64	..	...	...	...
	14.11	..	35.41	40.02	202.8
	...	..	36.02	40.15	202.0
Calcd.	14.18	9.60	35.84	40.38	197.9

The fluorochlorobromides of silicon are colorless, mobile liquids, which hydrolyze instantly when their vapors are allowed to come into contact with moist air, resembling the other known fluorohalides of this element in this and other respects. They do not attack pure mercury at room temperature.[4]

The vapor pressure of silicon fluorodichlorobromide was measured by the static method, that of the fluorochlorodibromide was measured both by the static and by a dynamic method, previously described.[1] The plotting of log P against $1/T$ gave very satisfactory straight lines, and the pressure data are summarized in the following table.

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(4) A stopcock lubricant consisting of 95% white vaseline and 5% paraffin was found to be very satisfactory in resisting attack by these substances.

TABLE II

VAPOR PRESSURE DATA

Substance	B. p., °C.	Log P	ΔH, cal.	Trouton's constant
$SiFClBr_2$	59.5	$7.5669 - (1558/T)$	7,095	21.38
$SiFCl_2Br$	35.4	$7.0982 - (1301/T)$	5,954	19.30

The melting points were determined by the method described by Skau,[5] the specimens being sealed in wafer-thin ampoules provided with thermocouple wells in which a copper–constantan thermocouple was inserted. Heating and cooling curves were then taken potentiometrically in the Skau apparatus. The melting points so determined are −112.3 ± 0.2° and −99.3 ± 0.2° for $SiFCl_2Br$ and $SiFClBr_2$, respectively.

Summary

1. Two fluorochlorobromides of silicon have been prepared for the first time, silicon fluorochlorodibromide, $SiFClBr_2$, and silicon fluorodichlorobromide, $SiFCl_2Br$. These substances are the first halides of silicon to be reported in which silicon is linked to three different halogen atoms.

2. The new compounds were prepared by three methods: the fluorination of silicon chlorobromides, the chlorination of silicon fluorotribromide, and the reaction of antimony trichloride with silicon fluorotribromide. The formulas of the compounds were established by analysis and molecular weight determinations.

3. $SiFClBr_2$ is a colorless, mobile liquid of b. p. 59.5°, m. p. −99.3°. Its vapor pressure is represented by the equation, $\log P = 7.5669 - (1558/T)$. $SiFCl_2Br$, also a colorless, mobile liquid, boils at 35.4°, and melts at −112.3°. Its vapor pressure is given by the equation, $\log P = 7.0982 - (1301/T)$.

4. Both liquids hydrolyze completely in moist air. In ice-cold water the hydrolysis products are silicic, hydrochloric, hydrobromic and hydrofluoric acids, with practically no fluosilicic acid.

5. Incidental to the main objective of the work, several new methods of preparing the three chlorobromides of silicon were developed, including the reaction of antimony trichloride or phosphorus trichloride with silicon tetrabromide; the refluxing of silicon tetrabromide for forty-eight hours in a sealed container in an atmosphere of chlorine; and the reaction of hexachlorodisilane with bromine.

CAMBRIDGE, MASS.

RECEIVED FEBRUARY 10, 1937

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[5] Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

[CONTRIBUTION FROM THE COMMITTEE ON DETERMINATION OF GEOLOGIC TIME, DIVISION OF GEOLOGY AND GEOGRAPHY, NATIONAL RESEARCH COUNCIL]

Atomic Weight of Lead from Galena, Great Bear Lake, N. W. T., Canada

BY JOHN PUTNAM MARBLE[1]

The fundamental assumption on which we base the "lead-ratio" method for measuring geologic time is that a given mineral has neither lost nor gained lead, uranium, or thorium since its first crystallization. As the writer recently pointed out,[2] further evidence on this point, either general or specific, is greatly desired in determining the age of the pitchblende at Great Bear Lake, Canada.

One of the mineral systems at this locality is a replacement band of sulfides in the country rock, which is cut by the pitchblende veins. Mr. Hugh S. Spence of the Mines Branch, Canada Department of Mines kindly furnished a generous sample of this material, with the following description:[3]

"Fine-grained galena from chalcopyrite-galena band in the country rock, cut by the No. 2 Vein at LaBine Point, Great Bear Lake, N. W. T., in the No. 2 pit on the easterly (siliceous) portion of the vein. The pieces were taken from the band approximately at the contact with the vein, and the galena carries some fine native silver, presumably introduced from the vein."

The question at once arises: "Is the lead in this ore 'common' lead, 'uranium' lead, or a mixture of the two?" If the first, it offers a source for the "common" lead found in the pitchblende;[4] if the second or third, it indicates that more or less lead may have been leached from the pitchblende, which would make it valueless as an "age-index" mineral.

Preliminary work showed that if the sample contained uranium or thorium, the amounts were too

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[1] Research Associate, Committee on Determination of Geologic Time.

[2] J. P. Marble, THIS JOURNAL, **58**, 434 (1936).

[3] Personal communication; *see also* H. S. Spence, Sec. III, Investigations in Min. Res. and Mining Indus., Ottawa, 1931, p. 61.

[4] (a) J. P. Marble, THIS JOURNAL, **56**, 854 (1934); (b) F. W. Aston, *Proc. Roy. Soc.* (London), **A140**, 535 (1933); (c) F. Hecht and E. Kroupa, *Z. anorg. allgem. Chem.*, **226**, 248 (1936).

TABLE I

$PbCl_2/2Ag$ AND ATOMIC WEIGHT OF LEAD FROM GREAT BEAR LAKE GALENA

Anal. no.	Vac. wt. $PbCl_2$, g.	Vac. wt. Ag, g.	Ag added in soln., g.	Corr. wt. Ag, g.	$PbCl_2/2Ag$	Atomic weight
I	0.54549	0.42293	+0.00025	0.42318	1.28903	207.206
II	2.77993	2.15663	± .00000	2.15663	1.28902	207.204
IV	1.17288	0.90980	+ .00010	0.90990	1.28902	207.205
				Average	1.28902	207.205

Total $PbCl_2$ = 4.49830. Total Ag = 3.48971. $PbCl_2/2Ag$ = 1.289018.
Atomic Weight Pb = 207.205.

small to detect by careful qualitative tests on a fair-sized sample, and a radiograph produced no trace of darkening on a photographic plate in forty-eight hours. A quantitative determination by the sulfate method showed 15.53% lead, and since over 100 g. was available, the lead was extracted, purified, and its atomic weight determined to see if an answer to the above question could be obtained.

The greater part of the sample was broken up on a clean hardened steel anvil, coarsely ground with a hardened steel muller, and finely powdered in a clean agate mortar. The powder in separate portions was decomposed with aqua regia, and the lead precipitated as sulfate, which was then extracted with hot ammonium acetate solution. A very small residue was decomposed by hydrofluoric acid, and a trace of lead recovered in the same way. The lead was then precipitated as sulfide, which was dissolved in hydrochloric acid, and again precipitated as sulfate. After several repetitions of this cycle, the lead was precipitated as sulfide from acid solution, again dissolved in hydrochloric acid, converted to nitrate, repeatedly crystallized as nitrate with centrifugal draining, converted to chloride, repeatedly crystallized as chloride, distilled in pure dry hydrogen chloride, and finally fused in pure dry hydrogen chloride, cooled in pure dry nitrogen and bottled in pure dry air in a Richards bottling apparatus. The water, acids and ammonia used were redistilled according to the customary Harvard technique, and hydrogen sulfide was obtained from cylinders of the purest commercial gas. Except for the sulfide precipitations, all operations were carried out in quartz or platinum.

The weighed sample was dissolved in warm water containing 1 or 2 drops of dilute nitric acid, and the chloride precipitated with purest silver in the dark room. The final concentration of lead and silver was about 0.03 *N*. The end-point was adjusted by equal opalescence nephelometry in the usual way. Weighings were made in duplicate by substitution on a sensitive balance at virtually constant temperature, using weights standardized by the Richards method. Vacuum corrections of +0.000058 g. per gram for lead chloride and −0.000031 g. per gram for silver were applied. The silver used had been found adequately pure in other atomic weight investigations.

The weight of lead chloride in Analysis III, made on the same portion as Analysis II, was incorrectly recorded due to an accident, and this analysis is omitted from the calculations. As a large part of the first lot worked up was lost by accident, Analyses II and IV were made on further portions of the sample. The method of purification was essentially the same for each.

The results of this work are in agreement with the most recent values for the atomic weight of "common" lead, by the chloride–silver ratio,[5] and indicate that the lead from this sulfide replacement band contains virtually no "uranium" lead. The possibility that we have a balancing of "uranium" and "thorium" leads to give the observed value is most improbable, as there is neither uranium nor thorium present in the ore, and the pitchblende at Great Bear Lake is essentially thorium-free. From this we may perhaps draw the following conclusions.

1. At Great Bear Lake there are at least two separate sources of mineralizing solutions, which have had little effect on each other, either during or after the first periods of deposition.
2. The pitchblende has not lost appreciable quantities of lead by leaching, as "uranium" lead has not travelled into the galena.
3. The small amount of "common" lead in the pitchblende may perhaps have come from the nearby galena, which might thus be older than the pitchblende.

General Conclusions

This work may be considered from another point of view as adding one more to the list of determinations of the atomic weight of "common" lead, in which the geologic provenance and horizon of the material is known, as shown in Table II.[6] This table lists only those determinations made on material of known provenance, using the ratio $PbCl_2/2Ag$, so as to provide a standard of comparison. In all cases the methods used for the purification of the lead chloride and the determination of the ratio have been described in sufficient detail to allow an evaluation of the precision

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(5) Report of International Committee on Atomic Weights, THIS JOURNAL, **59**, 219 (1937).

(6) Some of the earlier determinations are also listed in A. Holmes, Bull. 80, Nat. Res. Counc., p. 218, Washington, D. C., 1931.

TABLE II

ATOMIC WEIGHT OF "COMMON" LEAD

Mineral		Locality	Geologic age	Atomic weight
Cerussite	(1915)[a]	British Broken Hill Mine, N. S. W.	Pre-cambrian	207.21
Galena	(1915)[a]	Joplin, Mo., U. S. A.	Post-carboniferous	207.22
Cerussite	(1915)[a]	Wallace, Idaho, U. S. A.	Tertiary	207.21
Cerussite	(1915)[a]	Commern, Eifel Mts., Germany	Carboniferous	207.20
Galena	(1915)[a]	Grube Holzappel, Lahn, Germany	Carboniferous	207.21
Wulfenite and Vanadinite	(1915)[a]	Tucson Mts., Arizona, U. S. A.	Tertiary	207.22
Galena	(1915)[a]	Metalline Falls, Washington, U. S. A.	Tertiary?	207 21
Complex sulfides	(1931)[b]	Coeur d'Alene district, Idaho, U. S. A.	Tertiary	207.22
Complex sulfides	(1933)[c]	Coeur d'Alene district, Idaho, U. S. A.	Tertiary	207.21
Galena	(1935)[d]	Yancey County, N. C., U. S. A.	Pre-cambrian	207.21
Galena	(1936)[4c]	Tetüche, U. S. S. R.	Permian	207.22
Galena	(1937)	Great Bear Lake, N. W. T., Canada	Early? Pre-cambrian	207.21

[a] Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915). [b] Baxter and Bliss, *ibid.*, **52**, 4848 (1930). [c] Baxter and Alter, *ibid.*, **55**, 2785 (1933). [d] *Ibid.*, **57**, 467 (1935).

of the work. The total variation, 2 parts in 20,000, is close to the limit of error of careful nephelometric titration, especially when small samples of lead chloride have been taken. No evidence is present of any variation of the atomic weight of "common" lead as a function of geologic age. It seems worth while making this point, as Vernadsky[7] has recently brought up the question as to the constancy of atomic weight of various elements once more.

One further point may perhaps be made, but with extreme caution. The constancy of the atomic weight of "common" lead indicates that it probably cannot have been formed by processes of radioactive decomposition in the crust of the earth, with the generated lead removed and concentrated away from its parents by processes of solution and subsequent precipitation or crystallization. Since uranium and thorium have different half-lives, lead formed by radioactive decomposition at different times would have a varying isotopic composition and hence a varying atomic weight. If such a process is responsible for the formation of "common" lead, it must have taken place during "pretelluric" time, when the earth had no solid crust containing radioactive elements disintegrating as such in place. There seems to be little unequivocal cosmic evidence for such a process, as distinct from the processes by which other elements came into being. This leads to the conclusion that "common" lead owes its existence as such to the ordinary cosmic processes, whatever they may be, while leaving still unexplained the reason for the chemical identity of this element with the stable end-products of radioactive disintegration.

Acknowledgments.—Especial thanks are due to the Director of the U. S. Geological Survey, and to Professor Gregory P. Baxter of Harvard University, for permitting the use of their laboratories for this investigation. Dr. R. C. Wells of the Survey coöperated in the preliminary investigations, and Dr. J. H. Faull, Jr. and Mr. F. D. Tuemmler at Harvard aided in the purification of reagents and the setting up of apparatus. Professor Alfred C. Lane, Chairman of the Committee on the Measurement of Geologic Time, has provided constant inspiration.

Summary

1. The atomic weight of lead from galena at Great Bear Lake is 207.21.

2. The "common" lead contaminating the "uranium" lead of the pitchblende may have come from this source.

3. Presumably the pitchblende has not lost appreciable quantities of lead by leaching.

4. Further evidence is presented as to the constancy of the atomic weight of "common" lead as a function of its geologic age.

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RECEIVED FEBRUARY 10, 1937

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[7] V. I. Vernadsky, *C. R. Acad. Sci. U. S. S. R.* [N. S.], **3**, 129 (1936).

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Reaction between Hydrogen and Oxygen above the Upper Explosion Limit[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

The application of the isothermal chain-branching theory to the explosion limits of hydrogen and oxygen makes it necessary to ascribe to the reaction above the upper limit a different mechanism than that which governs the limits themselves.[4] Moreover, since the theory demands that the chain-breaking reactions be of the same order, with respect to the chain carriers, as the chain-branching reactions, and since plausible branching reactions are all of the first order with respect to the carriers, the most plausible reaction for breaking chains in the gas phase becomes

$$H + O_2 + M = HO_2 + M \tag{1}$$

M being any third molecule. This demands that the reaction between HO_2 and H_2 to form another chain carrier shall be a rare event in comparison with such reactions of HO_2 from which no chain carrier emerges.

It may now be assumed that in the low-pressure region where the limits occur, HO_2 is removed efficiently by diffusion to the wall but that at higher pressures there is an increasing probability for either or both of the chain continuing reactions

$$HO_2 + H_2 = H_2O_2 + H \tag{2}$$
$$HO_2 + H_2 = H_2O + OH \tag{3}$$

This conception makes it unnecessary to resort to the hypothesis of energy chains, the difficulties of which have been amply dealt with elsewhere.[5]

The necessity to introduce reaction (1) as a chain-breaking mechanism was originally demonstrated in a study of the inhibition of the photochemical reaction of hydrogen and chlorine by oxygen,[6] although it is to be remembered that the temperature in these experiments was low. More recently it has been shown that the formation of HO_2 in a ternary collision adequately accounts for the photochemical oxidation of HI[7] and that the earlier concept of a long-lived excited HO_2 molecule formed in a binary collision[8] should be abandoned. This latter fact uniquely determines from the "catalog" of possible reactions[4] the chain mechanism responsible for the explosion limits. The reactions are

$$H + O_2 = OH + O \tag{4}$$
$$O + H_2 = OH + H \tag{5}$$
$$OH + H_2 = H_2O + H \tag{6}$$

to which must be added the ternary reactions

$$H + O_2 + H_2 = H_2O_2 + H \tag{7}$$

and

$$H + O_2 + H_2 = HO_2 + H_2 \tag{1a}$$

which are contained in the "catalog" in their kinetic equivalents. Therefore, H_2 is able either to react or to stabilize the HO_2 molecule. The selection of reaction (7) instead of the alternative $H + O_2 + H_2 = H_2O + OH$ must be made on the basis of the results of the mercury-sensitized hydrogen–oxygen reaction.[9] Reaction (7) also harmonizes the results of the photochemical hydrogen–chlorine–oxygen reaction.[10] As far as can be seen, there is no contradictory evidence in the literature to any of the proposed reactions.[11]

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(1) Published by permission of the Director, U. S. Bureau of Mines, and the Director, Coal Research Laboratory, Carnegie Institute of Technology. Read at the meeting of the American Chemical Society, Pittsburgh, Pa., Sept., 1936. (Not subject to copyright.)

(2) Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

(3) Physical chemist, Explosives Division, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

(4) L. S. Kassel and H. H. Storch, THIS JOURNAL, **57**, 672 (1935); G. H. Grant and C. N. Hinshelwood's, *Proc. Roy. Soc.* (London), **141A**, 29 (1933) attempt to describe the limits and the reaction above the upper limit was shown by Kassel and Storch to be incorrect.

(5) C. N. Hinshelwood and A. T. Williamson, "The Reaction Between Hydrogen and Oxygen," Oxford Univ. Press, Oxford, England, 1934.

(6) *Cf.* M. Bodenstein and P. W. Schenck, *Z. physik. Chem.*, **B20**, 420 (1933).

(7) G. A. Cook and J. R. Bates, THIS JOURNAL, **57**, 1775 (1935).

(8) J. R. Bates and G. I. Lavin, *ibid.*, **55**, 81 (1933).

(9) J. R. Bates, *J. Chem. Phys.*, **1**, 457 (1933). This author's successful description of the mercury-sensitized reaction by assuming the consecutive steps

$$H + O_2 = HO_2$$
$$HO_2 + H_2 = H_2O_2 + H$$
$$HO_2 + HO_2 = H_2O_2 + O_2$$

may be duplicated by substituting the above ternary collision reactions (1a) and (7) for the first two steps.

(10) M. Bodenstein and P. W. Schenck's[6] mechanism requires that as a consequence of a successful collision between $H + O_2 + H_2$ two chains must be broken and two molecules of H_2O must be formed. For this reason they originally objected to the reaction products being $H_2O_2 + H$ as in Bates' scheme[9] since the H is capable of continuing the chain, and adopted instead the products $H_2O + OH$. Later, however, they postulate (p. 439) that for every H_2O_2 molecule formed, two chains are broken and two molecules of H_2O are formed by a series of reactions involving two chlorine atoms and two HCl molecules. Indeed, they prove that H_2O_2 readily reacts with chlorine atoms (p. 440). Thus their claim to be able to distinguish between the two mechanisms ($H_2O_2 + H$ or $H_2O + OH$) and their objection to Bates' scheme may be considered withdrawn.

(11) Reaction (4) has an energy of activation of at least 13 kcal., since it is endothermic to this extent. Reaction (5) also possesses a considerable energy of activation [Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931)]. Experiments of Kistiakowsky [THIS

The description of the explosion limits follows the treatment of Kassel and Storch.[4] For a given temperature the upper limit is reached when

$$2k_4 = k_1(\mathrm{M})\,^{12} \tag{8}$$

Frost and Alyea's[13] lower limit equation determined in a potassium chloride-coated vessel is obtained and Hinshelwood and Moelwyn-Hughes,[14] lower limit equation determined in a silica vessel can be approximated if it is assumed that on a silica surface H, O and OH are destroyed at the same rate, whereas on a potassium chloride surface H is destroyed[15] preferentially.

For the reaction rate above the upper explosion limit it is necessary to introduce the chain-initiating reaction. A decision must first be made whether chains are initiated at the surface or in the volume of the vessel. It has been demonstrated[16] that up to 540° at pressures below the upper explosion limit (20 to 100 mm.) two streams of hydrogen and oxygen may be crossed at some distance from the nozzles without inflaming, and that inflammation will occur if a silica rod is inserted at the junction of the streams; an aluminum rod was ineffective. These experiments were not extended to temperatures at which the gas would inflame in the absence of a surface. It has been demonstrated,[17] however, that streams of hydrogen and oxygen will inflame without the aid of a surface when crossed at atmospheric pressure and 560°. Of the different initial conditions in these two sets of experiments, namely, temperature and pressure, the former must be assigned a greater role. Thus, it appears that between 540 and 560° chain initiation becomes appreciable in the gas phase.

The reaction rate above the upper explosion limit has been studied largely with quiescent gas mixtures in vessels of silica and porcelain. If it is tentatively assumed that in the usual sized vessels volume initiation becomes predominant over surface initiation from 540 to 560° upward, then the observations made in such vessels on the effect on inert gases, the influence of diameter, the order of reaction, and the absence of any effect of poisoning the surface may be explained. There are, however, other experimental facts not easily explained on the basis of this assumption. These will be discussed more advantageously after the silica and porcelain vessel experiments have been treated in the light of the above hypothesis.

Chain Initiation in the Gas Phase

For reasons given below only the spontaneous formation of hydrogen atoms need be considered as a chain-initiating reaction. Their rate of formation per unit volume is denoted by I_{H}. Chains are broken by diffusion of HO_2 to, and their destruction at, the wall.

$$\mathrm{HO_2} \xrightarrow{\text{surface}} \text{destruction} \tag{9}$$

For the kinetic treatment the same formal result will be obtained by the use of either reaction (2) or (3), provided hydrogen peroxide decomposes to form water. It is thus sufficient to consider only one of them, say reaction (3).

From reactions (1), (3), (4), (5), (6) and (9) the expression for the reaction rate above the upper explosion limit is easily shown to be

$$\frac{\mathrm{d(H_2O)}}{\mathrm{d}t} =$$

$$I_{\mathrm{H}}\,\frac{2k_3(\mathrm{H_2})(\mathrm{M})d^2 + \dfrac{2k_4}{k_1(\mathrm{M})}\,(k_3(\mathrm{H_2})(\mathrm{M})d^2 + k_9)}{k_9\left(1 - \dfrac{2k_4}{k_1(\mathrm{M})}\right) - \dfrac{2k_4}{k_1}\,k_3(\mathrm{H_2})d^2} \tag{10}$$

k_1, k_3, etc., being the velocity coefficients of reactions (1), (3), etc., and *d* the diameter of the vessel. It is assumed here that the gas is quiescent and that the rate of diffusion is inversely proportional to the total pressure and inversely as the square of the vessel diameter, an assumption that is ideally true only if the chain carriers are not reflected from the walls,[4] but which holds with suffi-

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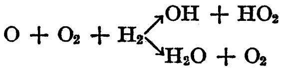
JOURNAL, **52**, 1868 (1930)] and Smith and Kistiakowsky [*ibid.*, **57**, 835 (1935)] with photochemically generated oxygen atoms in hydrogen–oxygen mixtures at room temperatures and pressures of the order of one atmosphere can be interpreted according to these authors, by



$$\mathrm{O + O_2 + H_2} \begin{cases} \nearrow \mathrm{OH + HO_2} \\ \searrow \mathrm{H_2O + O_2} \end{cases}$$

the competing reaction (5) being too slow under these conditions. These facts, however, do not make it improbable that reactions (4) and (5) should become sufficiently fast at the high temperatures in question in the present paper. For the same reason, it may be proposed that reaction (6) is so fast here that the recombination $OH + OH + M = H_2O_2 + M$ is slow in comparison. (For the requirement of a third body in the recombination of two OH, see Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935).) The inclusion of reaction (6) in Smith and Kistiakowsky's reaction scheme appears to furnish a suitable representation of the water yields obtained by these authors. These yields increase with lower total pressure, but not at the expense of either the ozone or hydrogen peroxide yields. Reaction (6) predicts this effect, short chains being formed, whose length increases toward lower pressures because of the decreased probability of the OH recombination reaction.

[12] This follows from Kassel and Storch's equation 19 if the constants k_1, k_{12} and k_{13} equal zero.

[13] A. A. Frost and H. N. Alyea, THIS JOURNAL, **55**, 3227 (1933).

[14] C. N. Hinshelwood and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **138A**, 311 (1932).

[15] The unsatisfactory state of our knowledge of the lower limit makes further elaboration inadvisable.

[16] H. N. Alyea and F. Haber, *Z. physik. Chem.*, **B10**, 193 (1930).

[17] F. Goldman, *ibid.*, **B5**, 316 (1929).

cient accuracy provided $\lambda/\epsilon r$ is small compared with 1.[18] λ is the mean free path, r the radius of the vessel, and ϵ the fraction of collisions of chain carriers with the wall that lead to destruction.

From equation (10) the condition for explosion is given by

$$k_9\left(1 - \frac{2k_4}{k_1(\mathrm{M})}\right) - \frac{2k_4}{k_1}\,k_3(\mathrm{H_2})d^2 = 0 \qquad (11)$$

which may be written in the form

$$k_1(\mathrm{M}) = 2k_4\left(1 + \frac{k_3(\mathrm{H_2})}{k_9/(\mathrm{M})d^2}\right) \qquad (12)$$

This agrees with the relationship (8) for the upper explosion limit if $k_9/(\mathrm{M})d^2 \gg k_3(\mathrm{H_2})$; that is, if at the upper limit the assumption made earlier holds, namely, that reaction (3) is a rare event compared with the destruction of HO_2 at the wall.

As the pressure is raised somewhat above the upper limit, the reaction rate drops sharply to small values as equation (11) increases rapidly from zero to finite positive values. On increasing the pressure still further, $2k_4/k_1(\mathrm{M})$ becomes small compared with 1, and $(2k_4/k_1)k_3(\mathrm{H_2})d^2$ increases until eventually a third explosion limit is reached at approximately

$$k_9 = (2k_3k_4/k_1)(\mathrm{H_2})d^2 \qquad (13)$$

It is doubtful that the observed third explosion limit is governed exactly by this condition. It is more likely that explosion occurs already at some lower pressure due to the very rapid increase of the reaction rate with pressure, which destroys the isothermal condition (see also reference 5).

For the further comparison of the theoretical expression for the reaction rate above the upper limit with experiment, it is necessary to introduce specific assumptions concerning the chain-initiating reaction. Experiments show that an increase in the oxygen concentration has no more effect than the addition of an equal amount of nitrogen,[5] that is, the oxygen concentration as such does not enter into the expression for the reaction rate. There remain, therefore, as initiating reactions only the formation of hydrogen atoms by dissociation of hydrogen and the formation of hydroxyl and hydrogen atoms or of oxygen atoms by dissociation of water. In initially dry mixtures the second reaction can be appreciable only after the reaction has progressed for some time. An accelerating influence of water actually has been observed.[5] It is to be noted, however, that part of the accelerating effect of water, as that of other inert gases, is caused by the change in diffusion characteristics due to different molecular weights and diameters; that is, k_9 is decreased. It is easily shown that the radical HO_2 should diffuse through oxygen about as readily as through water. However, the accelerating influence of water has been found to be considerably in excess of that of oxygen. Thus, the possibility that part of the accelerating effect of water is due to the above initiating reaction may remain open to consideration.

Assuming that a fraction of collisions of H_2 with other molecules leads to dissociation, the rate of chain initiation is given by

$$I_\mathrm{H} = k_{14}(\mathrm{H_2})(\mathrm{M}) \qquad (14)$$

A corresponding expression would apply for the water dissociation.

Equations (10) and (14) determine the change in reaction rate with the total pressure, the partial pressure of hydrogen and the vessel diameter at constant temperature. Whereas, at the upper limit itself the order of the reaction is minus infinity, the order increases continuously with rising pressure depending on the values of $2k_4/k_1(\mathrm{M})$ and $2k_4/k_1k_3(\mathrm{H_2})d^2$, until at the third explosion limit it becomes plus infinity.

The variable order is fully supported by experiment. For example, for a stoichiometric hydrogen–oxygen mixture at 569° the upper explosion limit was found to be at about 120 mm., almost unaffected by the size or material of the vessel,[19] as demanded by equation (12). In a porcelain bulb having a capacity of 200 cc. the order of the reaction rose from 2.6 at 225 mm. to over 6 at 600 mm.[20] The third explosion limit (not determined) was at a pressure above 600 mm.[20] Similar results were found in a silica vessel at 567°.[21]

Since k_3 and k_4/k_1 increase markedly with temperature the order of the reaction changes more rapidly with pressure at higher temperatures in agreement with experiment.[20,21] At a given pressure an increase in temperature may result in an increase or a decrease in the order depending upon the relative importance of k_3 and k_4/k_1, that is, upon the location of the pressure and temperature of the mixture with respect to the upper limit.

Reaction rates have been determined in silica vessels of different sizes from 1.7 to 7.7 cm. in diameter using stoichiometric mixtures at 300

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[18] G. von Elbe and Bernard Lewis, "The Steady State Rate of a Chain Reaction for the Case of Chain Destruction at Walls of Varying Efficiencies" submitted.

[19] H. W. Thompson and C. N. Hinshelwood, *Proc. Roy. Soc.* (London), **122**, 610 (1929).

[20] C. H. Gibson and C. N. Hinshelwood, *ibid.*, **119**, 591 (1928).

[21] C. N. Hinshelwood and H. W. Thompson, *ibid.*, **118**, 170 (1928).

and 600 mm. pressure at 560°.[5] The rate was found to increase approximately with the square of the diameter, a relation that may be obtained from equation (10) if $2k_4/k_1(\mathrm{M}) \ll 1$ and $\frac{2k_4}{k_1} k_3(\mathrm{H_2})d^2 \ll k_9$ and $k_3(\mathrm{H_2})(\mathrm{M})d^2 \gg \frac{k_4 k_9}{k_1(\mathrm{M})}$. These experiments are in an intermediate pressure range between the upper and third explosion limits characterized by an order of about four.[21] The fact that the proportionality of the rate with d^2 has been observed over a considerable range of pressure and vessel diameter can be considered to justify the assumption that the chain-breaking efficiency of the wall is not very small, thus allowing neglect of $\lambda/\epsilon r$ compared with 1, as has been done in deriving equation (10). It may be pointed out that for chain-breaking efficiencies less than 100%, the theory[18] predicts that the ratio, reaction rate/d^2, shall be constant only over a limited range of diameters, increasing toward small as well as large diameters. The minimum becomes more pronounced toward larger values of $\lambda/\epsilon r$, that is, lower pressures. Therefore, it is of interest to reproduce the experimental results of Williamson, Pickles and Hinshelwood,[5] in the following table.

TABLE I

REACTION RATE IN SILICA BULBS OF STOICHIOMETRIC MIXTURES OF HYDROGEN AND OXYGEN AT 560°

	d, mm.	17	32	56	77
Initial pressure 600 mm.	Rate/d^2	0.0030	0.0034	0.0030	0.0057
Initial pressure 300 mm.	Rate/d^2	.00062	.0005	.0003	.00058

Furthermore, reaction rates have been determined[20] in the intermediate pressure range by adding increasing amounts of hydrogen to a constant amount of oxygen, or *vice versa*, or by adding an inert gas like nitrogen to a mixture of hydrogen and oxygen. In order to compare these results with those derived from equation (10) it is necessary to consider, in addition to the inert gas effect expressed by the variable (M) in equation (10), the change in the diffusion characteristics of the mixtures due to differences in molecular weights and molecular diameters. An exact expression for the diffusion of $\mathrm{HO_2}$ through a mixture of hydrogen and oxygen and sometimes a third gas cannot be given. However, one may determine the diffusion coefficient of a hypothetical gas having an average molecular weight and diameter depending on the mole fraction, f, of hydrogen. The average molecular weight $\overline{m}$ of a mixture of hydrogen and oxygen may be given by $2f + 32(1 - f)$ and the average molecular diameter $\sigma_{\mathrm{av.}}$ by $f\sigma_{\mathrm{H_2}} + (1 - f\sigma_{\mathrm{O_2}})$. $\sigma_{\mathrm{HO_2}}$ may be identified with $\sigma_{\mathrm{O_2}}$. If a third inert gas is present the average molecular weight and diameter are calculated in a corresponding way. The substitution of this hypothetical gas should not be seriously in error, especially when relative rates are compared. Equation (10) reduces to

$$\frac{\mathrm{d(H_2O)}}{\mathrm{d}t} = \text{const.}\ \frac{(\mathrm{H_2})^4}{f^2} \frac{\bar{\sigma}^2}{\sqrt{\frac{1}{m_{\mathrm{HO_2}}} + \frac{1}{\overline{m}}}} \left[f\sigma^2_{\mathrm{H_2}} \sqrt{\frac{1}{m_{\mathrm{H_2}}}} + (1 - f)\sigma^2_{\mathrm{H,O_2}} \sqrt{\frac{m_{\mathrm{H_2}} + m_{\mathrm{O_2}}}{m_{\mathrm{H_2}} m_{\mathrm{O_2}}}}\right] \quad (15)$$

where $\bar{\sigma} = {}^1/_2(\sigma_{\mathrm{HO_2}} + \sigma_{\mathrm{av.}})$.

The following table contains the observed and calculated ratios of the reaction rates at the pressures indicated in the first two columns for different mixtures.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED RATIOS OF REACTION RATES

Oxygen pressure = 100 mm. 569°. $\sigma_{\mathrm{O_2}} = \sigma_{\mathrm{HO_2}} = 2.93 \times 10^{-8}$ cm.; $\sigma_{\mathrm{H_2}} = 2.36 \times 10^{-8}$ cm.[22]

Increase in $\mathrm{H_2}$ pressure, mm. From	To	Ratio of reaction rates Obsd.	Calcd.
200	300	3.0	3.3
300	400	2.8	2.5

Hydrogen pressure = 300 mm. 569°.

Increase in $\mathrm{O_2}$ pressure, mm. From	To	Ratio of reaction rates Obsd.	Calcd.
100	200	2.4	2.0
200	250	1.5	1.3

Hydrogen pressure = 300 mm. Oxygen pressure = 100 mm. 569°. $\sigma_{\mathrm{N_2}} = 3.10 \times 10^{-8}$ cm.[22]

Increase in $\mathrm{N_2}$ pressure, mm. From	To	Ratio of reaction rates Obsd.	Calcd.
0	100	2.3	2.0
100	150	1.4	1.3

Hydrogen pressure = 300 mm. Oxygen pressure = 150 mm. 569°. $\sigma_{\mathrm{He}} = 1.89 \times 10^{-8}$ cm.[22]

Increase in He pressure, mm. From	To	Ratio of reaction rates Obsd.	Calcd.
0	300	2.45	2.51
300	500	1.59	1.55

Hydrogen pressure = 200 mm. Oxygen pressure = 100 mm. 559°. $\sigma_{\mathrm{A}} = 2.84 \times 10^{-8}$ cm.[22]

Increase in A pressure, mm. From	To	Ratio of reaction rates Obsd.	Calcd.
0	200	5.24	2.78
200	500	2.71	2.78
500	700	1.35	1.64

The agreement is good, on the whole, considering the uncertainties in the underlying assumptions.

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(22) R. C. Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, Appendix 3.

In the range of gas-phase chain initiation a change in the character of the surface should have little or no effect on the reaction rate under the conditions of the foregoing experiments, since $\lambda/\epsilon r \ll 1$. Whereas coating a surface with potassium chloride strongly inhibits the reaction under conditions of predominance of surface initiation (Pease[23]), such coating, according to unpublished experiments referred to by Hinshelwood and Williamson,[5] has "failed to reveal any effect on the reaction in a silica vessel under conditions corresponding to most of the experiments" described in this section of gas-phase initiation.

Chain Initiation at the Wall

A plausible assumption concerning the surface initiating reaction is that H_2O_2 formed catalytically at the wall dissociates sometimes into 2OH.[23] Thus

$$H_2 + O_2 \xrightarrow{\text{Surface}} (H_2O_2) \longrightarrow 2OH \qquad (16)$$

If I_{OH} denotes the rate of chain initiation per unit area and γ is the ratio of surface to volume of the vessel, then $\gamma\, I_{OH}$ is the rate of chain initiation per unit volume.

If $K(HO_2)$ denotes the rate per unit volume of destruction of HO_2 at the surface, then reactions (1), (3), (4), (5), (6), (9) and (16) lead to the following relation between initiation, branching and breaking of chains

$$\frac{k_1(M)}{k_1(M) - 2k_4}\gamma I_{OH} + \frac{2k_4}{k_1(M) - 2k_4}k_3(H_2)(HO_2) = K(HO_2) \qquad (17)$$

The first term in equation 17 is the equivalent of the rate of release of HO_2 from the surface.

In a spherical vessel

$$K = \frac{\epsilon r}{2\lambda}\left(\frac{\pi^2 D}{r^2} - \frac{2k_4}{k_1(M) - 2k_4}k_3(H_2)\right) \qquad (18)$$

where D is the diffusion coefficient.[24]

For π^2D/r^2 one may substitute $k_9/(M)d^2$, k_9 being the same as in equation (10). For $\epsilon r/2\lambda$ one may substitute $k\epsilon(M)d$. Therefore

$$K = k\epsilon(M)d\left(\frac{k_9}{(M)d^2} - \frac{2k_4}{k_1(M) - 2k_4}k_3(H_2)\right) \qquad (19)$$

The rate of formation of H_2O then becomes, for $\lambda/\epsilon r \ll 1$

$$\frac{d(H_2O)}{dt} = \frac{\gamma I_{OH}}{1 - \frac{2k_4}{k_1(M)}}\left[\frac{\left(1 - \frac{2k_4}{k_1(M)}\right)2k_3(H_2)d}{\epsilon k\left(k_9\left(1 - \frac{2k_4}{k_1(M)}\right) - \frac{2k_4}{k_1}k_3(H_2)d^2\right)} + 1\right] \qquad (20)$$

It is seen that the conditions for explosion remain the same as before.

According to equation (20), the reaction rate between the upper and third explosion limits again has a variable order, which increases with pressure, and for $2k_4/k_1(M) \ll 1$, that is, at pressures sufficiently above the upper limit, increases with temperature. This is in agreement with experiment.[19,20]

If the temperature is not much above 500°, the rate of the chain reaction given by equation (20) is unimportant compared with a catalytic water-forming surface reaction.[20,21] This catalytic surface reaction possibly involves the primary formation of hydrogen peroxide[23] and predominates up to much higher temperatures if the vessel is packed. It is of zero order in a Worcester porcelain vessel and of first order with respect to hydrogen in a silica vessel. In an unpacked Worcester porcelain vessel the order of the total reaction was found to be 0.6 at 506° and more than 2 at 529° at intermediate pressures[19] due to the increased part played by the chain reaction.

Over a temperature range 520 to about 560° at intermediate pressures a gradual increase in the temperature coefficient of the reaction rate was found.[20,21] This may be understood to reflect essentially the transition from surface initiation with low temperature coefficient to gas-phase initiation with high temperature coefficient, as is indicated by equations (20) and (10) for intermediate pressures.

Equation (20) indicates that the reaction rate should be independent of the diameter of the vessel at intermediate pressures. No experiments in this temperature–pressure range are available.

Further Discussion of Volume Initiation Versus Surface Initiation

Experiments on quiescent gas mixtures in a silver vessel up to 700°, that is, in a temperature

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[23] This would account for the observation of Pease [THIS JOURNAL, **52**, 5106 (1930)] that coating of the wall with potassium chloride slows down the reaction rate very markedly. Potassium chloride destroys peroxidic substances efficiently, as is borne out by Pease's and other authors' experiments on the oxidation of hydrogen, aldehydes and hydrocarbons (see von Elbe and Lewis, *ibid.* (in print), thus preventing the release of chain carriers from the wall. However, Pease's results may also be interpreted as being due to an increase in the efficiency of destruction of HO_2 on a potassium chloride surface. Some of Pease's experiments were conducted in a temperature range in which gas phase initiation would be expected to predominate. However, his experiments were made by a flow method, and the gases were far from quiescent. This has a dual effect. In the first place, it enhances the release of chains from the surface and, second, it increases the dependence of the rate of chain breaking on the efficiency of the wall beyond that obtaining were the transport of chain carriers to the wall governed solely by diffusion.

[24] See ref. 18. ϵ is assumed to be small compared with 1.

range where volume initiation was assumed to occur, show that the chain reaction is practically suppressed.[25] Even at temperatures at which the reaction has become very fast or even explosive in a silica vessel, only a slow catalytic surface reaction occurs in a silver vessel. If the initiation is occurring in the gas phase, these facts cannot be explained by the presumably very high efficiency of chain breaking at a silver surface, because an increase in the chain-breaking efficiency from a moderate value, such as is found in silica vessels, to perfect efficiency, should have, according to the theory, no pronounced effect on the reaction rate; this is different for surface initiation (compare equations 10 and 20 and also reference 18). If one attempts to attribute the above effects to high chain-breaking efficiency of a silver surface, one must reconsider the results obtained at high temperatures in silica and porcelain vessels on the basis of surface initiation. This leads to difficulties. In the first place, it is evident that surface initiation is inconsistent with the observation that coating of a silica vessel with potassium chloride does not affect the reaction in the high-temperature range. In the second place, equation (20) does not describe the facts concerning vessel diameter and inert gases.

A possible answer to this latter objection is that OH radicals that are formed by reaction (16) and for which a silica or porcelain but not a silver surface is highly reflective, may diffuse for a considerable distance, on the average, into the gas phase before they react to form HO_2. This would be equivalent to gas-phase initiation as far as inert-gas effect is concerned, but it would demand a dependence of the rate on d instead of d^2. It would also conflict with the fact that the introduction of a silica rod into a silver vessel failed to initiate reaction even at pressures and temperatures within the explosive region below the upper limit.[25] It will be recalled that a silica rod caused ignition in crossed stream experiments under similar conditions. Thus, one is faced with several new difficulties not accounted for by high chain-breaking efficiency of a silver surface.

This leads to an alternative hypothesis, namely, that in a silver vessel chain carriers are destroyed in the gas phase by the action of silver or some compound of silver in the vapor form. The presence of silver in the gas phase need not necessarily arise from the thermal evaporation of silver at the temperature of the experiments. It is well known that atomic hydrogen, for example, on recombining in contact with metals causes sputtering of the metal. This sputtering phenomenon has been observed especially well on silver.[26] In addition to the possible sputtering effect of atoms and radicals in a hydrogen–oxygen mixture, it is entirely possible energetically for the catalytic formation of water on the surface of silver to give rise to the same phenomenon. It may also be mentioned that in an atmosphere of pure hydrogen the volatility of silver is increased somewhat.[27]

Once this hypothesis is conceded,[28] then the assumptions made earlier in this paper regarding gas phase and surface initiation remain plausible. Should it fail and if all experimental observations mentioned in this paper are correct, then the treatment of the reaction between hydrogen and oxygen would require a radically new approach.

Summary

The only mechanism for the interaction of hydrogen and oxygen consistent with photochemical experiments (mercury-sensitized reaction, photoöxidation of hydrogen iodide, inhibition by O_2 of the photochemical reaction between hydrogen and chlorine) and experiments on the lower and upper explosion limits is

$$\begin{aligned} H + O_2 + M &= HO_2 + M \\ H + O_2 + H_2 &= H_2O_2 + H \\ HO_2 + HO_2 &= H_2O_2 + O_2 \\ H + O_2 &= OH + O \\ O + H_2 &= OH + H \\ OH + H_2 &= H_2O + H \\ H, O, OH + \text{surface} &\longrightarrow \text{destruction} \end{aligned}$$

to which is to be added the chain-initiating reaction at the surface or in the gas phase.

If it is now assumed that in the thermal reaction HO_2 is normally destroyed at the surface but at high temperatures and pressures is capable of undergoing reaction with H_2 to an appreciable extent either by

$$HO_2 + H_2 = H_2O_2 + H$$

or

$$HO_2 + H_2 = H_2O + OH$$

the reaction above the upper limit can be described adequately, provided chains are initiated

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(25) C. N. Hinshelwood, E. A. Moelwyn-Hughes and A. C. Rolfe, *Proc. Roy. Soc.* (London), **139**, 521 (1933).

(26) K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

(27) A. Farkas, *ibid.*, **5B**, 467 (1929).

(28) A number of experiments suggest themselves among which is the passage of cold streams of hydrogen, oxygen, and mixtures of these past a heated silver screen and noting the formation of a silver deposit.

predominantly in the gas phase above about 540–560°. The latter assumption makes it necessary to ascribe the suppression of the reaction in a silver vessel to gas-phase deactivation due to silver. This is discussed in some detail.

PITTSBURGH, PENNA. RECEIVED JANUARY 21, 1937

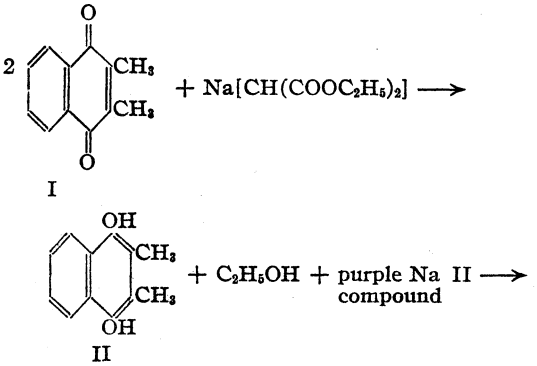
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

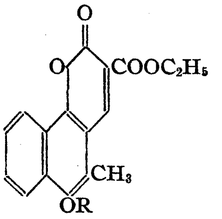
The Reaction between Quinones and Sodium Enolates. V. 2,3-Dimethylnaphthoquinone and Sodium Malonic Ester[1]

BY LEE IRVIN SMITH AND ISABELLA M. WEBSTER[2]

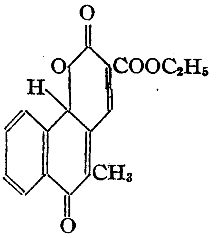
Previous papers in this series have dealt with the reaction between sodium enolates and two types of quinones: (1) duroquinone, a fully methylated para benzoquinone, and (2) trimethylquinone, a para benzoquinone with one unsubstituted position in the ring. In case 1, the reaction involved one of the methyl groups attached to the nucleus, and led ultimately to a coumarin derivative. In case 2 the reaction was most simply interpreted as involving an initial 1,4-addition of the reagent to the conjugated system which terminated in the unsubstituted position of the ring. In the latter case, the final products were benzofuran derivatives. In both cases only one molecule of reagent (sodium malonic ester) could be made to react.

In order to explore somewhat further the limits of the coumarin formation shown by duroquinone (case 1) the work described in this paper was undertaken and a benzolog of duroquinone, 2,3-dimethylnaphthoquinone (I), was selected for study. This quinone, like duroquinone, has two methyl groups attached to the quinone nucleus in positions 2 and 3, but positions 5 and 6, instead of holding methyl groups, are fused to a benzene ring. This quinone, if it were to react with sodium malonic ester in the same manner as duroquinone, should give rise to an intermediate sodium compound (II), which on hydrolysis would produce an α-naphthocoumarin derivative (III)[3] together with an equivalent amount of the hydroquinone.





III R = H
IV R = Ac



IIIa

This quinone, however, proved to be far more difficult to handle than duroquinone, and it was only after the original procedure used by Smith and Dobrovolny[4] had been modified considerably that a crystalline product could be obtained in good yield by decomposition of the sodium derivative II. In several experiments, the black quinhydrone derived from I was produced as a by-product. As this quinhydrone was apparently fairly stable in ether (the solvent used) it was necessary to allow time for the air to oxidize it back to the quinone in order to obtain the maximum yield of III from I, otherwise 3 moles of I were required to produce 1 mole of III.

The product III formed fine yellow needles melting at 212–213° with decomposition, and it had the composition and molecular weight corresponding to the formula $C_{17}H_{14}O_5$. No carbonyl derivatives could be formed using hydroxylamine or 2,4-dinitrophenylhydrazine, but the presence of one hydroxyl group was shown by the formation

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[1] Paper IV, THIS JOURNAL, 58, 629 (1936).

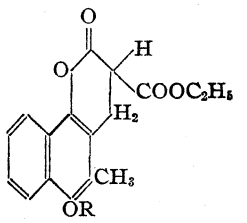
[2] Abstracted from a thesis by Isabella M. Webster, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1936.

[3] These compounds are more correctly termed 7,8-benzocoumarins. However, in the literature the term α-naphthocoumarin is used to designate them; therefore this term will be used throughout this discussion.

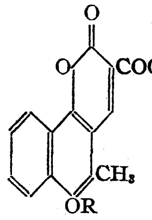
[4] Smith and Dobrovolny, THIS JOURNAL, 48, 1701 (1926).

of a pale greenish-yellow monoacetate (IV). The failure of the carbonyl reagents to react indicated that the structure was III, rather than IIIa, and the fact that the acetate IV was colored showed conclusively that it was not necessary to postulate a tautomerism between IIIa and III to explain the color of these hydroxycoumarins or the lack of it when the hydroxyl group was fixed by acetylation or methylation.[4]

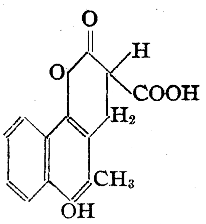
The double linkage in the pyrone ring was shown by the formation of a dihydro compound (V) when III was reduced catalytically: the dihydro compound V likewise formed a monoacetate (VI), and this same monoacetate VI was obtained when the acetate IV was reduced.



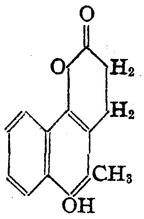
V $R = H$
VI $R = Ac$



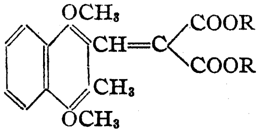
VII $R = H, R' = H$
VIII $R = Ac, R' = H$
XI $R = CH_3, R' = H$
XII $R = CH_3, R' = CH_3$



IX



X

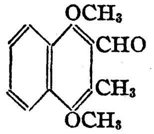


XIIa $R = CH_3$
XIIb $R = H$

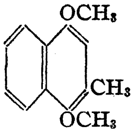
The formation of the same acetate VI regardless of whether reduction preceded or followed acetylation eliminated the possibility that the reduction had occurred at the carbonyl group of such a structure as IIIa and established the presence of a double bond in the pyrone ring of III.

The presence of the ester grouping in III was shown by the hydrolysis of III to the corresponding acid VII, which formed a monoacetyl derivative VIII. Catalytic reduction of the acid VII led to a mixture which contained at least two colorless substances. In analogy with the work of Smith and Denyes[5] this product is represented as a mixture of IX and X. These substances could not be separated by fractional crystallization, nor could IX be removed by shaking with any alkaline reagent because of the extreme ease with which the solutions were oxidized. For the same reason hydrolysis of V to IX was unsuccessful; the products in every case were yellow mixtures, and no better results were obtained when the acetate VIII was reduced. In none of these reductions, however, was there evidence of any substance which would correspond to the dimolecular products found by Smith and Denyes in the case of the coumarin from duroquinone.

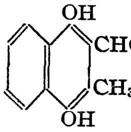
With a view to opening the coumarin ring so that the substance could be degraded further, several of the compounds in this series were methylated. It was hoped to prepare the dimethoxy compounds XIIa and XIIb, and to cleave one of these by oxidation to the aldehyde XVII which would then be synthesized. Although both methyl sulfate and methyl iodide were used, and, although the conditions were varied widely, all attempts to methylate the sodium derivative II, the ester III, the acetate IV, the acid VII or its barium salt, led only to the two methyl derivatives XI and XII, and attempts to methylate further these two products were unsuccessful. The hetero ring in this naphthocoumarin is therefore much more stable than is the case with the corresponding coumarin derived from duroquinone. The ester III reacted with diazomethane to give a *colorless* product, melting at 138–139°. From the analysis of this product, the lack of color (all of the compounds in this series except the reduced products are colored), and the reactions, it was obvious that the substance could not be either XIIa or XIIb. The substance was therefore not investigated further in connection with this work although a later research on the reaction between coumarins and aliphatic diazo compounds is planned.



XVII



XVI



XVIII

Since the coumarin ring could not be opened it was necessary to abandon further attempts at degradation, and to establish the coumarin struc-

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(5) Smith and Denyes, THIS JOURNAL, 58, 304 (1936).

ture by direct synthesis. It was first planned to synthesize the acid XIIb as this should melt with loss of methanol to give the monomethyl derivative XI. This synthesis was unsuccessful, for the diether XVI could not be prepared from either the hydroquinone XV or its diacetate (XIV). The hydroquinone–aldehyde XVIII was prepared from the hydroquinone (XV),[6] and this aldehyde when condensed with malonic ester led directly to the ester III; when the aldehyde was condensed with malonic acid, the product was the coumarin acid VII. The reactions of III and VII, together with the syntheses of these two products from the aldehyde XVIII, leave no doubt as to the structure of the products obtained from the reaction between 2,3-dimethylnaphthoquinone and sodium malonic ester. These products are coumarin derivatives, and the course of the reaction is entirely analogous to that of the reaction between duroquinone and sodium malonic ester. The most conspicuous differences between the two series of compounds lie in the much greater stability of the hetero ring in the naphthocoumarins and in the fact that *all* of the compounds in the naphthocoumarin series (except the reduced products) are colored.

Experimental Part[6a]

2,3-Dimethylnaphthoquinone (I).—The following directions for the preparation of this quinone were found to give consistent results and excellent yields (60–80%). To a solution of 2,3-dimethylnaphthalene (10 g.) in acetic acid (350 cc.) at room temperature was added with stirring a solution of chromic acid (25.6 g.) in dilute acetic acid (130 cc. acid, 35 cc. water). The temperature was kept between 20 and 30° throughout the addition of the chromic acid, which required about fifteen minutes. The reaction mixture, after standing at room temperature for three days, was diluted with about 1.5 liters of water and allowed to stand for several hours. The quinone was filtered and washed thoroughly with water. Crystallized from alcohol, the product melted at 126–127°. Contrary to the experience of Wieser[7] it was found that the acetic acid filtrate from the quinone contained only negligible amounts of material. Steam distillation of the quinone was found to be an unsatisfactory method of purification, for considerable amounts of tars and resins were formed and the loss was great. The best method found for purification was that of Fieser,[8] which gave a product melting sharply at 127°.

1,4 - Diacetoxy - 2,3 - dimethylnaphthalene (Ib).—The quinone I (0.3 g.) was dissolved in acetic acid (10 cc.) and zinc dust was added. To the resulting red solution was added acetic anhydride (10 cc.) and a drop of sulfuric acid and the mixture was refluxed until it became colorless (thirty minutes). The cooled solution was decanted from the zinc into excess water, and the zinc was washed with hot acetic acid which was poured into the water. The white crystals melted at 184–189°; after five recrystallizations from alcohol the product melted at 189–190°.[9]

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.55; H, 5.92. Found: C, 70.55; H, 5.99.

Quinhydrone (Ic) of 2,3-Dimethylnaphthoquinone.—The quinone I (1.86 g., m. p. 121–125°) was dissolved in acetic acid (10 cc.), zinc dust was added and the mixture was refluxed until it became colorless. Water was added, and the hydroquinone was filtered. When dissolved in methanol, the hydroquinone gave a deep purple solution from which a black solid melting at 129° was isolated. Crystallized several times from 50% acetic acid, the melting point rose to 134–138°. One preparation melted at 139–144°. The quinhydrone was very unstable, even in the solid state, yellow crystals of the quinone appearing on the surface after a day in a desiccator.

Addition of Sodium Malonic Ester to the Quinone.—To a warm solution of the quinone (4.65 g.) in absolute ether (160 cc.) was added with stirring a solution of sodium malonic ester (made from sodium (0.6 g.) dry ethyl alcohol (60–80 cc.) and malonic ester (4 g.)). The addition of the reagent required about one hour; the solution turned brown, then green. Refluxing (41–43°) and stirring were continued for five and one-half hours. After about one hour the purple color of the sodium derivative II began to appear and at the end of the reaction the green color had disappeared entirely. After standing for some time, the solvent was decanted (it contained chiefly quinone and quinhydrone) from the deep purple solid. The solid was transferred to a filter with ether, washed with a small amount of water and alcohol and a large amount of ether (300 cc.) and dried. It weighed 4.3 g. From the various filtrates and washings, about 25% of the quinone used was recovered.

5 - Methyl - 6 - hydroxy - 3 - carbethoxy - α - naphthocoumarin (III) was obtained when a suspension of the sodium derivative II (4 g.) in ethyl alcohol (50 cc.) was acidified with hydrochloric acid (10 cc.). The products were 3.05 g. of III melting at 208–211° and a dark, tarry solid which yielded about half a gram of quinone when steam distilled. The coumarin crystallized from absolute ethyl alcohol in yellow needles melting at 212–213°.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.43; H, 4.73; mol. wt., 298. Found: C, 68.39; H, 4.83; mol. wt. (Rast), 301, 299.

It was not necessary to isolate the sodium derivative, however, for the coumarin could be obtained by adding dilute acetic acid directly to the reaction mixture and allowing it to stand in the ice-box for some time. The product contained unchanged quinone, which was removed by boiling ether, and the residue, crystallized from absolute alcohol, melted at 211–213°. Often, especially when too much ether was used in the condensation, the quinhydrone Ic was recovered instead of the quinone.

The addition could also be carried out in dry benzene, according to the original method of Smith and Dobrovolny[4]

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[6] Madinaveitia, (a) *C. A.*, **29**, 3330 (1935); (b) *Rev. acad. cienc. Madrid*, **31**, 617–647 (1934).

[6a] Microanalyses by J. W. Opie.

[7] *Monatsh.*, **1**, 604 (1880).

[8] Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, 1935, pp. 230, 231.

[9] Crawford, THIS JOURNAL, **57**, 2000 (1935).

although the time required was long (seven days) and the yield was only about half that obtained by the procedure given above.

The coumarin III was decomposed by hydroxylamine in alkaline solution or in a solution buffered with sodium acetate, and no oxime could be obtained.

6 - Acetoxy - 5 - methyl - 3 - carbethoxy - α - naphthocoumarin (IV).—The coumarin III (1 g.) was refluxed in acetic anhydride for one hour and the solution then poured into water. The product, crystallized from acetic acid or absolute ethanol, weighed 0.9 g. and melted at 195–196°. It was pale greenish-yellow.

Anal. Calcd. for $C_{19}H_{16}O_6$: C, 67.09; H, 4.71. Found: C, 67.26; H, 5.05.

6 - Hydroxy - 5 - methyl - 3 - carbethoxy - 3,4 - dihydro-α-naphthocoumarin (V).—The coumarin (III) and about half its weight of a palladium catalyst[10] were suspended in ethanol or methanol and shaken with hydrogen under 35–40 pounds (1.16–1.34 atm.) until the mixture was colorless. The catalyst was allowed to settle, the supernatant liquid poured off through a filter, and the filtrate evaporated under reduced pressure. The product was recrystallized from ethanol, but it was necessary to exclude air as much as possible since the compound was readily oxidized. The substance was white and melted at 175–176°. Of the two solvents, ethanol was found to be much the better for the dihydro compound was much more readily oxidized in methanol than in ethanol.

Anal. Calcd. for $C_{17}H_{16}O_5$: C, 67.97; H, 5.37. Found: C, 67.70; H, 5.52.

6 - Acetoxy - 5 - methyl - 3 - carbethoxy - 3,4 - dihydro - α-naphthocoumarin (VI) was obtained when the acetyl derivative IV was reduced catalytically as above; the same product resulted when the dihydrocoumarin V was acetylated by refluxing with acetic anhydride for thirty minutes. Crystallized from alcohol, the substance was white, and the m. p. and mixed m. p. of specimens prepared by the two methods was 145–145.5°.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.27. Found: C, 66.34; H, 5.35.

6 - Hydroxy - 5 - methyl - 3 - carboxy - α - naphthocoumarin (VII).—The action of most hydrolyzing agents was accompanied by considerable decomposition and gave products which were very difficult to purify. This was especially true of 80% sulfuric acid, the reagent used by Smith and Dobrovolny[4] for hydrolysis of their ester. Sodium hydroxide caused complete decomposition and no hydrolysis product could be isolated. When applied to the *pure* ester, the following procedure was found to give good yields of a product which was readily purified. The ester III (3.6 g.) was suspended in acetone (150 cc.) and dilute hydrochloric acid (400 cc. 1:1) and the mixture was refluxed for eight hours. The mixture was then cooled and the solid filtered, washed with water and dried. It weighed 3.1 g. (95%) and formed fine orange needles melting (dec.) at 275–276° when the bath was preheated to 240° and at 263° (dec.) when the bath was at room temperature at the beginning. The acid was insoluble in benzene and petroleum ether, very slightly soluble in ether, alcohol, chloroform or ethyl acetate, and quite soluble in acetone. For recrystallization, which was difficult, acetic acid was the best solvent, although alcohol could be used.

Anal. Calcd. for $C_{15}H_{10}O_5$: C, 66.65; H, 3.73. Found: C, 66.60; H, 3.87.

Catalytic reduction of the acid VII in ethyl alcohol, using the method described for the reduction of the ester III, gave a colorless solution in about three hours. The solution acquired a yellow color when it was decanted from the catalyst through a filter. The solvent was evaporated to 15 cc. under reduced pressure and the solution allowed to stand, tightly stoppered, overnight. No solid separated during this time, but the solution turned deep red in color. The solvent was then evaporated completely, leaving a solid melting at 142° which was very soluble in all the common solvents except petroleum ether. Crystallization from chloroform–petroleum ether was accompanied by great losses of material and the product was tinged with red and could not be obtained pure. The highest melting point obtained was 153–161° (dec.) (IX?) and this material, after the melt had solidified, re-melted at 129–130° with no evolution of gas (X?). Although 1.4 g. of the acid VII was reduced, it was not possible to isolate from the product enough pure material for analysis. Catalytic reduction of the acid VII in sodium carbonate solution gave only red oils from which no solid could be obtained.

When the dihydro ester V was subjected to the procedure used for hydrolysis of the coumarin ester III, the colorless solution became first yellow and then orange. The solid which precipitated melted at 155–159°; addition of excess water to the cold filtrate gave a solid which melted at 120–125°. The amounts of both were very small.

6 - Acetoxy - 5 - methyl - 3 - carboxy - α - naphthocoumarin (VIII).—The acid VII was boiled for four hours with acetic anhydride, the orange color fading to yellow. The mixture was then poured into ice water and allowed to stand for some time. The product, crystallized from acetic acid, melted at 258° (dec.).

Anal. Calcd. for $C_{17}H_{12}O_6$: C, 65.37; H, 3.87. Found: C, 64.97; H, 3.87.

Catalytic reduction of this acetyl derivative in ethyl alcohol, using the palladium catalyst, gave only oils from which in only one of many experiments was any solid obtained and then in extremely small amounts.

6 - Methoxy - 5 - methyl - 3 - carboxy - α - naphthocoumarin (XI).—The coumarin acid VII (0.2 g.) in methyl sulfate (3–4 g.) and methanol (25 cc.) was refluxed while 20% aqueous potassium hydroxide was added in small portions. Each portion of the alkali caused a red color to develop, which then faded. When a color change no longer occurred, an excess of the alkali was added and the mixture was refluxed for fifteen minutes. The cold solution was acidified with sulfuric acid, sufficient water was added to dissolve the potassium salts, and the yellow insoluble precipitate was removed and crystallized several times from methyl alcohol. It melted at 222–225°, was soluble in ethyl alcohol, methyl alcohol, ether and chloroform and almost insoluble in benzene.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.58; H, 4.26; OCH_3 (one), 10.92. Found: C, 67.66, 67.55; H, 4.69, 4.61; OCH_3, 11.87.

Methylation of the ester III or the acetyl derivative IV in methyl sulfate, using the general procedure above and

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[10] Busch and Stöve, *Ber.*, **49**, 1064 (1916).

1% aqueous sodium hydroxide as the alkali, gave the same product (XI) in yields of about 70%.

6 - Methoxy - 5 - methyl - 3 - carbomethoxy - α - naphthocoumarin (XII).—The coumarin acid VII (1 g.) was dissolved in 4% sodium methoxide–methanol (6 cc.); heated gently for thirty min. (purple color) and cooled. Methyl sulfate (1 cc.) and 4% sodium methoxide–methanol (6 cc.) were then added and the flask shaken vigorously for ten minutes. The addition of like quantities of reagents at ten-minute intervals, with vigorous shaking in between, was continued until a total of 19 cc. of methyl sulfate and 114 cc. of the alkali were added, after which the mixture was allowed to stand for fifteen hours. Concentrated ammonia (5 cc.) and water (30 cc.) were added and the mixture warmed on the steam-bath for thirty minutes. An excess of water was then added, the solution cooled and the solid removed and crystallized from methanol. It melted at 182–183° and the yield was 90%. In ether the substance showed a green fluorescence. These directions had to be followed carefully, otherwise the product was a mixture of the ethers XI and XII which was very difficult to separate, or else only the mono-ester XI resulted. The hydrolysis of the ester group in XII occurred with great ease and in most methylation reactions only the monomethyl derivative XI resulted. The dimethyl derivative was somewhat less soluble in alcohol than the monomethyl derivative.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.46; H, 4.69; OCH_3 (two), 20.80. Found: C, 68.46; H, 4.78; OCH_3, 21.03.

The dimethyl derivative XII when refluxed for three to four hours with 10% aqueous potassium hydroxide gave a clear yellow solution, which on acidification gave the monomethyl derivative XI, m. p. and mixed m. p. 223–225°.

The dimethyl derivative XII was also obtained (impure, m. p. 175–177°, mixed m. p. 177–182°) when the purple sodium derivative II was suspended in methanol and refluxed with excess methyl iodide. This impure specimen of XII, when hydrolyzed, gave the methoxy acid XI, m. p. and mixed m. p. 221–223°.

Many other experiments were carried out in the attempt to open the coumarin ring of the ester III or the acid VII in the hope of obtaining the ester XIIa or the acid XIIb. The procedures of various authors[11] were tried several times. All of these methods, except the ones described above, gave the monomethyl derivative XI, unchanged material or decomposition products. The barium salt of the acid XI was prepared by the method of Marschalk[12] but when refluxed with methyl sulfate and methanol it charred completely.

Aside from the substances XI and XII, the only other methyl derivative obtained was by action of diazomethane upon the ester III. This reaction led to a *white* crystalline solid (from alcohol) which melted at 138.5–139° (dec.). The analysis indicated a carbon–hydrogen ratio of approximately 1:1; qualitative tests for nitrogen were negative. No satisfactory formula for this compound has as yet been written.

2-Methylnaphthoquinone (XIII).[13,6]—2-Methylnaphthalene (12.5 g.) was dissolved in acetic acid (118 cc.) and a suspension of chromic acid (50 g.) in 80% acetic acid (90 cc.) was added in a continuous stream. After the highly exothermic reaction was over, the mixture was allowed to stand for an hour and then was diluted with water. The yellow precipitate was removed, washed well with water, dissolved while still wet in ether and the ethereal solution was filtered and dried over calcium chloride. If the crude material was orange in color, the ethereal solution was treated with charcoal before drying it. Evaporation of the ether to crystallization yielded bright yellow needles; the yield was 25–40% and the product melted at 105–107°. The quinone could be purified by steam distillation or crystallization from alcohol or 50% acetic acid. It was unstable in the light, turning from yellow to a dull tan in color.

2-Methylnaphthohydroquinone.—The quinone XIII could be reduced by any of several methods, but the isolation of the product was difficult because of the extreme ease with which the hydroquinone was oxidized to the purple quinhydrone and then to the quinone. Catalytic reduction in ether or methanol with hydrogen under 40 pounds (1.34 atm.) pressure and in the presence of the palladium catalyst gave colorless solutions, which could be used directly if a solution of the hydroquinone were desired, but from which the pure solid hydroquinone was isolated only with difficulty. Reduction with zinc and sulfuric acid gave only deep red solutions and continued boiling with the reducing agent did not cause the color to disappear. Reductive acetylation of the quinone (10 g.) in acetic acid (25 cc.), acetic anhydride (100 cc.) and sodium acetate (5 g.) by refluxing the solution with zinc dust (10 g.) gave 1,4-diacetoxy-2-methylnaphthalene in 82% yield. Crystallized from methanol, the substance was white and melted at 112.5–114°.[13]

All attempts to prepare the dimethyl ether of the hydroquinone (XVI) led to red oils which distilled with complete decomposition.

1,4 - Dihydroxy - 3 - methyl - 2 - naphthaldehyde (XVIII).[5b]—The most successful procedure for this preparation consisted in the catalytic reduction of the quinone in absolute ether, and the use of the resulting ethereal solution of hydroquinone directly for introduction of the aldehyde group. The quinone (7.5 g.) was suspended in absolute ether (160 cc.), palladium catalyst (4 g.) was added and hydrogen passed in under 40 pounds (1.34 atm.) pressure. The color disappeared in five minutes, but the reaction was allowed to continue for about thirty minutes. The catalyst was allowed to settle, the solution was decanted, the catalyst was washed with absolute ether and the solution and washings were placed immediately in the reaction flask for the next step. Zinc cyanide (9.1 g.) was added, and with stirring and cooling (0°), dry hydrogen

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[11] (a) Meyer, *Monatsh.*, **24**, 837 (1903); (b) Perkin and Robinson, *J. Chem. Soc.*, **91**, 1079 (1907); (c) Decker and Koch, *Ber.*, **40**, 4794 (1907); (d) Freudenberg, *ibid.*, **53**, 1424 (1920); (e) Stoermer and Friemel, *ibid.*, **44**, 1843 (1911); (f) Stoermer and Friderici, *ibid.*, **44**, 644 (1911); (g) Tiemann, *ibid.*, **8**, 1135 (1875); (h) Chakravarti, *J. Ind. Chem. Soc.*, **7**, 247 (1930); (i) Houben–Weyl, "Die Methoden der org. Chem.," George Thieme Verlag, 1923, Vol. III, p. 11, 103; (j) Freudenberg, *Ann.*, **433**, 234 (1923); *Ber.*, **56**, 1191 (1923); (k) Haworth, *J. Chem. Soc.*, 2681 (1928); (l) Kohn and Grun, *Monatsh.*, **46**, 75 (1925); (m) Späth and Klager, *Ber.*, **67**, 859 (1934).

[12] Marschalk, *Ber.*, **45**, 585 (1912).

[13] (a) Fries and Lohmann, *Ber.*, **54**, 2912 (1921); (b) Madinaveitia and S. de Buruaga, *C. A.*, **24**, 359 (1930); (c) Anderson and Newman, *J. Biol. Chem.*, **103**, 406 (1933).

chloride was passed in rapidly until the solution became saturated (one and one-half hours) and then more slowly for two hours longer.[14] The milky solution gradually cleared and then an orange solid slowly separated. The ether was decanted, and after washing the solid with fresh ether it was warmed with water (50–100 cc.) until all the imide hydrochloride decomposed. The mixture was cooled and the aldehyde was removed and crystallized from 50% acetic acid, dilute alcohol or chloroform–petroleum ether. The yield was 5.6 g. (64%) and the melting point was 158–160°. The chief impurity in the crude aldehyde was a black substance (quinhydrone?). Steam distillation of the aldehyde gave only quinone in the distillate and a residue of red oil which solidified on cooling; vacuum distillation was also unsatisfactory as a method of purification. The aldehyde could not be converted into an oxime, but with aniline it gave a precipitate of beautiful red needles.

Condensation with Malonic Ester.—To the aldehyde (1.44 g.) in alcohol (2 cc.) there was added piperidine (0.76 g.) and ethyl malonate (2 cc.). The mixture was warmed on the steam-bath until a clear solution resulted, then set aside for a day. The product which had crystallized from the solution was allowed to stand with hydrochloric acid for fifteen to twenty minutes, filtered and washed with cold alcohol and ether. Crystallized from alcohol, the product weighed 0.43 g. and melted at 209–211°; the mixed melting point with a specimen of III (m. p. 208–209°) was 208–209°. Acetylation of this product gave the same acetyl derivative (IV) as was obtained from the ester III; m. p. and mixed m. p. 193–195°.

Condensation of the aldehyde (1 g.) with malonic ester (2 cc.) in acetic acid (2 cc.) led to a solid (0.05 g.) which was chiefly the acetyl derivative VIII. It melted at 248–253°; the mixed m. p. with VIII (m. p. 258°) was 246–250°.

Condensation with Malonic Acid.—To the aldehyde (1.4 g., crude) and malonic acid (0.7 g.) in dry methanol (7 cc.) was added one drop of piperidine and the solution was refluxed on the steam-bath for eighteen hours. A small amount of chloroform was added and the solution was filtered. The chloroform was evaporated from the filtrate, a little methanol was added and the yellow solid was filtered and washed with water and dilute hydrochloric acid. The solid melted at 273–275°; the mixed melting point with a specimen of the acid VII (m. p. 273–275°) was also 273–275° (copper block).

Summary

1. Sodium malonic ester reacts with 2,3-dimethylnaphthoquinone to give a purple sodium derivative which when treated with acid gives 5-methyl-6-hydroxy-3-carbethoxy-α-naphthocoumarin.

2. The physical and chemical properties of this coumarin and a number of its derivatives have been described, and the structure of the coumarin was proved by an independent synthesis from 1,4-dihydroxy-3-methyl-2-naphthaldehyde.

3. The course of the reaction between the methylated naphthoquinone and sodium malonic ester is entirely analogous to that between duroquinone and sodium malonic ester, but the hetero ring in the naphthocoumarin is much more resistant to opening by alkaline reagents.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 8, 1937

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[14] Adams and Levine, THIS JOURNAL, **45**, 2373 (1923).

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

The Reaction between Quinones and Sodium Enolates. VI. Duroquinone and Sodium Acetoacetic Ester[1]

BY LEE IRVIN SMITH AND DAVID TENENBAUM[2]

In the first paper of this series[3] it was shown that the fully methylated quinone, duroquinone, reacted with sodium malonic ester to give a coumarin derivative (I). In a later paper, Smith and MacMullen[4] showed that trimethylquinone, with one unsubstituted position in the ring, reacted with malonic ester and with acetoacetic ester to give benzofuran derivatives, malonic ester giving only one product (Ia), while acetoacetic ester gave two products (Ia and Ib). These products were the result of an initial 1,4-addition of the reagent to the quinone conjugated system which terminated in the free position, but this reaction was not accompanied by the oxidative step which occurred when the coumarin was formed from duroquinone. The fact that acetoacetic ester gave two products suggested a study of the reaction between this reagent and duroquinone. If the reaction followed the same course as that of malonic ester, the product would be the acetylcoumarin II; but there was also the possibility that the intermediate addition product (IIa) would be oxidized to a form which could undergo self-condensation leading to the *amphi*-naphthoquinone derivative IIb. These products would themselves be of interest,

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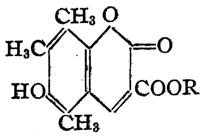
[1] Paper V, THIS JOURNAL, **59**, 662 (1937).

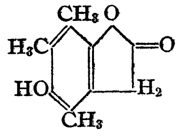
[2] Abstracted from a thesis by David Tenenbaum, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1936.

[3] Smith and Dobrovolny, THIS JOURNAL, **48**, 1693 (1926).

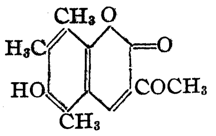
[4] Smith and MacMullen, *ibid.*, **58**, 629 (1936).



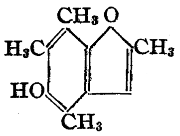
I R = C_2H_5
VI R = H



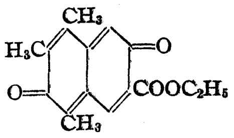
Ia



II



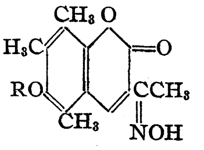
Ib



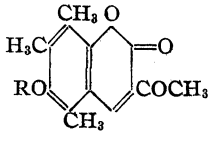
IIb

for few representatives of either acetylcoumarins or *amphi*-naphthoquinones are known; but, in addition, if the naphthoquinone derivative were formed, it might be possible, by a detailed study of the reaction, to gain some information as to the oxidative step in the process.

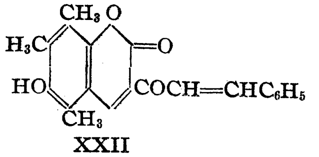
When duroquinone and acetoacetic ester were condensed according to the method of Smith and Dobrovolny[3] there resulted a *purple* sodium compound (IIa). The reaction mixture poured into iced hydrochloric acid gave a solid which crystallized from acetic acid in the form of tan needles melting at 222–226°. The wide melting point range of this substance and the failure to obtain concordant analyses led to the discovery that the substance held duroquinone tenaciously. When this was removed by treatment of the acetic acid solution with charcoal, a bright yellow substance (II), melting at 227–228°, was obtained. The substance had the composition $C_{14}H_{14}O_4$ corresponding to the acetylcoumarin II; it could be readily converted into a yellow oxime (III), a *colorless* acetyl derivative (IV), and a benzal derivative XXII.



III R = H
VIII R = CH_3



IV R = Ac
V R = Na
VII R = CH_3
XXI R = C_6H_5CO



XXII

It was not possible to obtain anything but high melting, amorphous products when the coumarin II was subjected to the action of methyl sulfate and potassium hydroxide in methanol, but aqueous sodium hydroxide (10%) converted the coumarin into a *red* sodium derivative, represented as V, and when methyl iodide, or better methyl sulfate, was added to this sodium derivative suspended in methanol, the methoxy compound VII separated in the form of pale *yellow* needles. The red sodium compound V, refluxed with a solution of benzoyl chloride in benzene, gave the benzoate XXI.

Catalytic reduction of the coumarin II led to a dihydro compound (XVI) which formed an oxime (XVII), as well as an acetyl derivative (XVIII), and could be methylated with methyl sulfate and potassium hydroxide to give the methyl ether XIX. Reduction of the acetyl derivative IV also gave XVIII, and similarly reduction of the methyl ether VII gave XIX—that is, the same methyl or acetyl derivative resulted regardless of whether reduction preceded or followed methylation or acetylation. These reactions proved the presence of a double bond in the coumarin II and also proved conclusively that reduction of the acetylcoumarin involved only the double bond. The methyl derivative XIX gave an oxime (XX), but the acetyl derivative XVIII gave the hydroxy oxime XVII, the acetyl group being removed during the reaction between XVIII and hydroxylamine.

Numerous attempts were made to oxidize the acetylcoumarin II by hypohalites, and thus convert it into the carboxycoumarin VI, a known substance prepared several years ago by Smith and Dobrovolny.[3] But the acid VI was itself attacked by hypohalites, and in only one case, by action of sodium hypobromite on the red sodium compound V, was it possible to isolate the acid VI in quantity sufficient for identification.

The reactions given so far indicated quite clearly the structure of the product from the reaction between duroquinone and sodium acetoacetic ester, but the final proof of this structure was furnished by an independent synthesis of the acetylcoumarin II. Dimethoxydurylic aldehyde[5] was condensed with acetoacetic ester. Unfortunately neither the benzalacetoacetic ester nor the acid obtained from it by hydrolysis could be made to crystallize. Nevertheless, when the resulting oil

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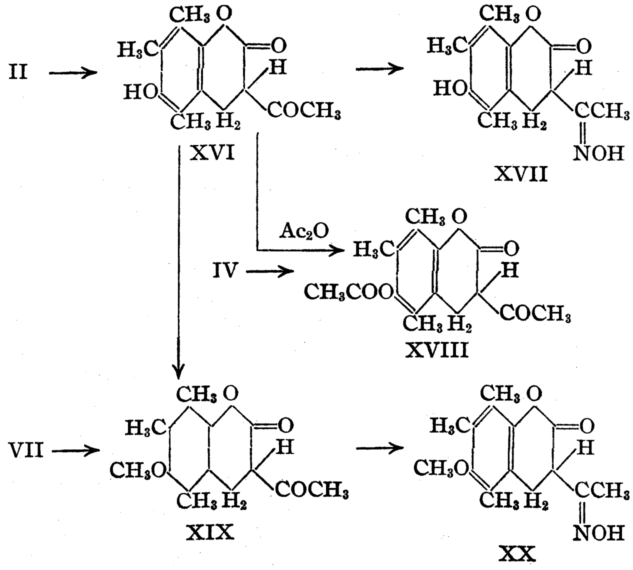
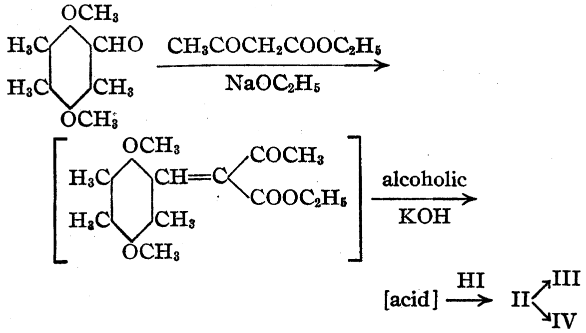
[5] Smith, THIS JOURNAL, **56**, 472 (1934).



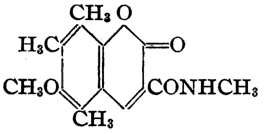
was boiled with hydriodic acid, it gave the acetylcoumarin II, and the synthesized coumarin gave the same oxime and acetyl derivative as those given by the coumarin obtained from duroquinone and sodium acetoacetic ester.

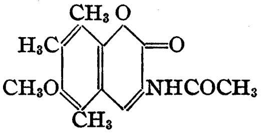


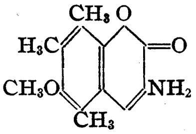
Hence the reaction between duroquinone and sodium acetoacetic ester follows the same course as that taken by this quinone and sodium malonic ester. The product is 5,7,8-trimethyl-3-acetyl-6-hydroxycoumarin and half of the quinone is converted to the hydroquinone. The failure to obtain any *amphi*-naphthoquinone derivative (IIb) from the reaction shows that the oxidation is confined to the side chain (or coumarin ring) of the product.

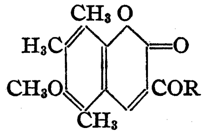
Since the oximes III and VIII were obtained readily, considerable study was devoted to their behavior in the Beckmann rearrangement. The oxime III did not react with sulfuric acid below 100°; above that temperature complete decomposition resulted. Both phosphorus pentachloride and benzene sulfonyl chloride reacted, but the resulting product was a mixture from which no pure compounds could be separated. The methoxy oxime VIII was more tractable, and when it was treated with benzene sulfonyl chloride and pyridine, an isomer resulted. Depending upon the configuration of the oxime VIII, structures IX or X were possible for this product.

Since the quantity of material was small, no attempt was made to hydrolyze this product until after the methyl amide IX was synthesized from the acid XI[3] via the acid chloride. The methyl amide IX so obtained was different from the rearrangement product of the oxime VIII. The structure of the latter was therefore strongly indicated to be X, a result in agreement with the work of Linch[6] who found that the oximes of 3-acetylcoumarin and 6-bromo-3-acetylcoumarin, when rearranged, gave the corresponding acetylaminocoumarins rather than the methyl amides of the coumarin acids. When hydrolyzed, the rearrangement product gave a crystalline compound containing nitrogen, the analysis of which corresponded to that required by formula XII, 3-amino-6-methoxy-5,7,8-trimethylcoumarin. Attempts were made to convert the acid XI into XII and so prove the structure X. The hydrazide (XIV) and the hydroxamic acid (XV) of XI were prepared, but these could not be rearranged. Attempts to prepare XII via the azide (XIII) of XI were also made, but neither the procedure of Newman[7] nor that of Nelles[8] was successful. The only product isolated was a non-basic substance containing nitrogen (XIII?) which melted at 210° with violent decomposition.


IX


X


XII


XI R = OH
XIII R = N_3
XIV R = $NHNH_2$
XV R = NHOH

In spite of failure to synthesize the amine XII, it is felt that the non-identity of the rearranged

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(6) Linch, *J. Chem. Soc.*, **101**, 1761 (1912).

(7) Newman, THIS JOURNAL, **57**, 732 (1935).

(8) Nelles, *Ber.*, **65**, 1345 (1932).

product with IX, together with its reactions, point fairly conclusively to structure X. If then the Beckmann rearrangement of the oxime VIII is a *trans* migration, it follows that the configuration of the oxime is as represented in formula VIII with the hydroxyl group *anti* to the coumarin ring.

Experimental Part

The Addition Reaction: 3-Acetyl-6-hydroxy-5,7,8-trimethylcoumarin, (II).—Acetoacetic ester (80 g.) was added in small portions to a suspension of powdered sodium (13 g.) in boiling benzene (1000 cc.). The addition of the ester required forty-five minutes, after which the mixture was refluxed, with frequent shaking, for two hours. Duroquinone (35 g.) dissolved in dry benzene (400 cc.) was added and the mixture refluxed for eight days. The color of the solution changed from yellow through brown to reddish-brown, and a purple solid (IIa) precipitated. The entire reaction mixture was poured into hydrochloric acid (500 cc.) and ice (500 g.). The tan solid was removed, washed twice with benzene and dried *in vacuo*. It was crystallized twice from acetic acid using Norite, which removed unchanged duroquinone. The product crystallized in bright yellow needles melting at 227–228°. It was insoluble in petroleum ether, benzene or methanol; difficultly soluble in boiling ethanol, chloroform or cold acetic acid. The yield of tan solid was 20 g.; that of the purified product was 12 g.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.29; H, 5.69. Found: C, 68.05, 67.97; H, 5.61, 5.88.

3 - Acetyl - 6 - acetoxy - 5,7,8 - trimethylcoumarin (IV) resulted when the coumarin II (1 g.) was warmed with acetic anhydride (10 cc.) and a drop of sulfuric acid. Crystallized from acetic acid (with charcoal to remove the dark color) the product formed pale yellow needles melting at 201–202.5°. The yield was 0.8 g.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.64; H, 5.60. Found: C, 67.00; H, 5.70.

3 - Acetyl - 6 - benzoyl - 5,7,8 - trimethylcoumarin, (XXI).—The purple sodium compound IIa from the reaction between duroquinone and acetoacetic ester was filtered and triturated twice with benzene. The salt (0.5 g.) was suspended in a solution of benzoyl chloride (2 cc.) in benzene (10 cc.) and the mixture refluxed for three hours. Unchanged salt (0.25 g.) was filtered off and the filtrate was stirred vigorously into water. Ether was added and the layers were separated. Evaporation of the organic layer left an oily residue containing benzoyl chloride, which was decomposed by adding alcohol and allowing to stand for five hours. The white solid was removed and crystallized from alcohol (using Norite). It weighed 0.12 g. and melted at 162–163°.

Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.97; H, 5.18. Found: C, 71.45; H, 5.49.

The oxime III resulted when the coumarin II (0.2 g.) was suspended in water (2 cc.) and ethanol (5 cc.) containing hydroxylamine hydrochloride (0.5 g.) and sodium hydroxide (2 cc., 10%) and the mixture warmed on the steam-bath for ten minutes. The oxime formed long, pale yellow needles melting at 258–260° (dec.). The yield was 0.2 g. The same oxime III resulted when the acetyl derivative IV reacted with hydroxylamine.

Anal. Calcd. for $C_{14}H_{15}O_4N$: C, 64.34; H, 5.79. Found: C, 63.92; H, 6.18.

The oxime III could not be made to undergo the Beckmann rearrangement. Benzene sulfonyl chloride in pyridine, as well as phosphorus pentachloride in ether, gave only impure amorphous products; sulfuric acid, at room temperature or at 100°, was without action.

Synthesis of II.—To the solution obtained by dissolving sodium (0.1 g.) in methanol (15 cc.) were added acetoacetic ester (1 cc.) and dimethoxydurylic aldehyde (0.5 g.). The mixture was warmed until the aldehyde dissolved and then allowed to stand at room temperature for three days. Water was added and the mixture was steam distilled. Dimethoxydurylic aldehyde (0.2 g.) was recovered from the distillate. The residual alkaline solution was acidified, extracted with ether (three times) and the ether was evaporated. As the oily residue could not be made to crystallize it was dissolved in ethanol (5 cc.) and boiled for ten minutes with potassium hydroxide (1 g.) in ethanol (10 cc.).

The solution was diluted with water, acidified, extracted with ether and the ether evaporated. The product was again an oil, which was warmed for an hour with constant boiling hydriodic acid (2 cc.). The solution was poured into ice water, and the precipitate was removed and crystallized from acetic acid with the aid of a little Norite. The product (0.2 g.) formed bright yellow needles melting at 226–227°; when mixed with the coumarin II from duroquinone, the melting point was 226–227°. The oxime melted at 257–260° (dec.), and when mixed with the oxime III the melting point was 257–260° (dec.).

Oxidation of II to VI.—To a solution of sodium hydroxide (3.4 g.) in water (30 cc.) was added the coumarin II (1 g.). The red sodium salt (V) precipitated. Bromine (1.8 cc.) was dropped slowly into the cold, stirred suspension of the sodium salt. Bromoform was removed by extracting with ether, and bisulfite was added to remove the excess hypobromite. The solution was acidified, extracted three times with ether and the ether evaporated. The residue was an orange oil which slowly deposited a small amount of solid. Washing with ethanol removed the oil, and the residual solid was crystallized from acetic acid. The product weighed 0.05 g., and the melting point was 260° (dec.). The mixed melting point with a specimen of 3-carboxy-6-hydroxy-5,7,8-trimethylcoumarin (VI) (m. p. 256–257°, dec.) was 257–260° (dec.). No other solid could be isolated; the low yield was due to the fact that VI was itself oxidized by hypobromite, giving only oils and bromoform (odor).

3 - Acetyl - 6 - methoxy - 5,7,8 - trimethylcoumarin, (VII).—The usual procedures for methylation with methyl sulfate and alkali failed when applied to the coumarin II but the methyl derivative VII was obtained as follows: the sodium salt V was precipitated by suspending the coumarin II (0.64 g.) in sodium hydroxide (20 cc., 10%). The salt V was filtered, washed several times with cold acetone and suspended in methanol (50 cc.). Methyl sulfate (3 cc.) was added with shaking. In about three minutes the red color changed to yellow and the methoxy compound began to crystallize. The product was filtered, suspended in ether and extracted several times with sodium hydroxide (2%) to remove unchanged II. From the ether solution was obtained 0.41 g. of the methoxy compound VII melting at 158.5–159.5° and crystallizing in long, pale yellow needles.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.23; H, 6.15. Found: C, 69.26; H, 6.30.

Oxidation of the methyl derivative VII by hypoiodite or by hypobromite gave iodoform (or carbon tetrabromide) and either unchanged VII or else only oily tars.

3 - Benzalacetyl - 6 - methoxy - 5,7,8 - trimethylcoumarin, (XXII).—To the methoxycoumarin VII (0.56 g.) and benzaldehyde (5 cc.) in methanol (30 cc.) was added dilute sodium hydroxide (5 cc.) and the mixture was refluxed for three hours. The product was obtained by acidifying with acetic acid (3%), diluting with water and cooling. Crystallized from methanol, it melted at 187–189° and weighed 0.28 g.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.83; H, 5.79. Found: C, 75.45; H, 6.12.

Treatment of the benzal derivative with chromic acid in acetic acid in the cold gave unchanged material as the only isolable product; when the reaction mixture was warmed, the substance was oxidized completely.

The oxime VIII resulted when the methoxycoumarin (VII) (0.2 g.) was warmed for ten minutes with hydroxylamine hydrochloride (0.5 g.), water (1.5 cc.), sodium hydroxide (1.5 cc., 10%) and methanol (5 cc.). Crystallized from toluene, it weighed 0.18 g., and formed white needles melting at 225–227° (dec.).

Anal. Calcd. for $C_{15}H_{17}O_4N$: C, 65.42; H, 6.23. Found: C, 65.34; H, 6.68.

Beckmann Rearrangement: 3-Acetylamino-6-methoxy-5,7,8-trimethylcoumarin, (X).—To a solution of the oxime VIII (0.175 g.) in dry pyridine (2 cc.) was added benzene sulfonyl chloride (2 cc.). A dark brown color developed at once. After standing at room temperature (26°) for three hours, the solution was poured into ice (5 g.) and hydrochloric acid (5 g.). The mixture was extracted with ether and the ether, as well as the suspended solid, washed with water. Both the ether and the water were filtered and the solids were combined and crystallized from methanol. A second crop was obtained by concentrating the ether solution. The product weighed 0.075 g., melted at 237–238°, and formed long white needles. The mixed melting point with the oxime VIII (m. p. 225–227°, dec.) was 190–195°.

Anal. Calcd. for $C_{15}H_{17}O_4N$: C, 65.42; H, 6.23. Found: C, 65.74; H, 6.60.

3 - Amino - 6 - methoxy - 5,7,8 - trimethylcoumarin, (XII).—The acetylaminocoumarin X (0.04 g.) was refluxed with hydrochloric acid (6 *N*, 15 cc.) for fifteen minutes. The cooled solution was neutralized with sodium carbonate and the precipitate taken up in ether. The ether was evaporated and the residue crystallized from aqueous methanol. The product weighed 0.02 g., and melted at 150–151°.

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.92; H, 6.49; N, 6.00. Found: C, 66.62; H, 6.70; N, 6.40.

Methylamide of 3-Carboxy-6-methoxy-5,7,8-trimethylcoumarin, (IX).—The methoxy acid[3] (p. 1706) (1 g.) was warmed with thionyl chloride (5 cc.) and the thionyl chloride was then removed under reduced pressure, leaving a pale yellow solid. This was dissolved in dry benzene (5 cc.) and methylamine was passed into the solution. The yellow color disappeared and a white solid precipitated. The solvent was evaporated and the product crystallized from dilute acetic acid. It weighed 0.85 g., and melted at 214–215°. The mixed melting point with X (m. p. 237–238°) was 205–207°.

Anal. Calcd. for $C_{15}H_{17}O_4N$: C, 65.42; H, 6.23. Found: C, 65.28; H, 6.23.

Attempts to Prepare the Aminocoumarin, XII.—A chloroform solution of hydrazoic acid was prepared[7] using technical sodium azide (0.15 g.) and sulfuric acid (0.6 cc.). This solution was added dropwise, with stirring, to a solution of the methoxy acid XI (0.56 g.) in sulfuric acid (5 cc.) at a temperature of 40°. No gas was liberated; after standing for thirty minutes the mixture was poured onto ice. The only product was unchanged acid XI.

The methoxy acid XI (0.5 g.) was refluxed for one hour with thionyl chloride (5 cc.) and the excess thionyl chloride then removed under reduced pressure. The acid chloride was taken up in dry benzene and stirred for two hours with activated sodium azide.[8] No gas was evolved. Hydrochloric acid (10 cc.) was then added and the mixture was refluxed for an hour. Evaporation of the solvents left an oily material from which no pure product could be isolated. Repetition of the experiment, heating the acid chloride with sodium azide at 50°, gave a small amount (0.12 g.) of white solid which could not be purified. It melted at about 210° with violent decomposition, and was unaffected by boiling with hydrochloric acid in acetone.

The methoxy acid XI (0.5 g.), sodium azide (1 g.) and sulfuric acid (5 cc.) were sealed in a Carius tube and heated at 150° for an hour. The material was recovered unchanged.

Hydrazide of 3-Carboxy-6-methoxy-5,7,8-trimethylcoumarin, (XIV).—To a suspension of the methoxy acid XI (0.5 g.) in alcohol (10 cc.) was added with shaking, a few drops of hydrazine hydrate solution (40%). The white solid, crystallized from alcohol, weighed 0.5 g. and melted at 184–185° with violent decomposition.

Anal. Calcd. for $C_{14}H_{16}O_4N_2$: C, 60.84; H, 5.84. Found: C, 60.48; H, 6.10.

The hydrazide (0.25 g.) in ether was stirred with a solution of sodium nitrite (0.5 g.) in water (10 cc.). To the mixture, at 5°, was added slowly hydrochloric acid (6 *N*, 2 cc.). No product, other than a small amount of unchanged hydrazide, could be isolated and the same result was obtained when the experiment was repeated substituting acetic acid for the ether.

Hydroxamic Acid of 3-Carboxy-6-methoxy-5,7,8-trimethylcoumarin, (XV).—The acid XI (0.25 g.) was suspended in alcohol and hydroxylamine hydrochloride (0.5 g.) was added. Sodium hydroxide (3%) was dropped in slowly and with shaking, until a faint alkaline reaction resulted. The solution was acidified with dilute acetic acid (5%), an equal volume of water was added and the mixture was allowed to stand for several hours. The product, crystallized from aqueous alcohol, was pale yellow, melted at 236–237° and weighed 0.15 g.

Anal. Calcd. for $C_{14}H_{15}O_5N$: C, 60.62; H, 5.46. Found: C, 60.39; H, 5.70.

The hydroxamic acid was recovered unchanged after boiling in acetone and acetic anhydride.

3 - Acetyl - 6 - hydroxy - 5,7,8 - trimethyl - 3,4 - dihydrocoumarin (XVI).—The coumarin II (0.5 g.) and a palladium catalyst (0.5 g.)[9] were suspended in alcohol (100 cc.) and the solution was subjected to the action of hydrogen under 45 pounds (3.0 atm.) pressure. Reduction was complete in forty-five minutes. The solution was decanted from the catalyst and diluted to three times its volume with water. The product, crystallized from petroleum ether–benzene, weighed 0.45 g. and formed white needles melting at 164–165°.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.71; H, 6.50. Found: C, 67.36; H, 6.85.

Methylation.—A solution of potassium hydroxide (5 g.) in methanol (25 cc.) was added dropwise to the boiling solution of the reduced coumarin XVI (0.2 g.) in methanol (10 cc.) and methyl sulfate (5 cc.). The reaction was stopped as soon as the red color remained permanent for about ten seconds. Most of the methanol was evaporated, water was added and the solution was extracted with ether. Evaporation of the ether left an oily solid which was digested with dilute ammonium hydroxide (3%) to remove excess methyl sulfate. The solid, crystallized from aqueous alcohol, weighed 0.05 g. and melted at 111–113°. It was identical (m. p. and mixed m. p.) with the product XIX obtained by reduction of VII.

Acetylation.—The dihydrocoumarin XVI (0.25 g.) was warmed for thirty minutes with acetic anhydride (5 cc.) and sulfuric acid (2 drops). The reaction mixture was poured into ice water and the product was crystallized from aqueous alcohol. It weighed 0.15 g., and melted at 123–125°. It was identical (m. p. and mixed m. p.) with the product XVIII obtained by reduction of the acetyl derivative IV.

The oxime XVII resulted when the hydrocoumarin XVI (0.2 g.) followed by sodium hydroxide (1 cc., 10%) was added to a suspension of hydroxylamine hydrochloride (0.5 g.) in alcohol (10 cc.). After warming on the water-bath the solution was filtered and the filtrate concentrated to half its volume. Water (10 cc.) was added and the solution was cooled. The product (0.2 g.) crystallized from aqueous alcohol, formed long white needles melting at 179–180° (dec.).

Anal. Calcd. for $C_{14}H_{17}O_4N$: C, 63.85; H, 6.51. Found: C, 63.47; H, 6.81.

3 - Acetyl - 6 - methoxy - 5,7,8 - trimethyl - 3,4 - dihydrocoumarin, (XIX).—Catalytic reduction of the methoxycoumarin VII (0.5 g.) by the method described above gave 0.5 g. of the dihydro compound XIX. Crystallized from aqueous alcohol, the substance melted at 112–113.5°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.67; H, 6.92. Found: C, 68.39; H, 7.23.

The oxime XX, prepared in the same manner as XVII, crystallized from aqueous methanol in colorless needles melting at 156–157° (dec.).

3 - Acetyl - 6 - acetoxy - 5,7,8 - trimethyl - 3,4 - dihydrocoumarin, (XVIII).—Catalytic reduction of the acetyl derivative IV (0.25 g.) in ethanol (75 cc.) by the method described above gave 0.24 g. of the dihydro compound XVIII. Crystallized from aqueous alcohol, it melted at 124–125°.

Anal. Calcd. for $C_{16}H_{18}O_5$: C, 66.17; H, 6.25. Found: C, 65.93; H, 6.25.

Summary

1. Sodium acetoacetic ester has been added to duroquinone. The reaction follows the same course as that of the reaction between this quinone and malonic ester, and involves one of the methyl groups of the quinone.

2. The product is a methylated 3-acetyl-6-hydroxycoumarin; no evidence of any naphthoquinone derivative was obtained. The structure of the coumarin was proved by an independent synthesis.

3. Several reactions of the coumarin and its derivatives were investigated, particularly the Beckmann rearrangement of the oxime of the methoxycoumarin, which led to an aminocoumarin, indicating that the hydroxyl group was *anti* to the coumarin ring in this oxime.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 10, 1937

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[9] Busch and Stöve, *Ber.*, **49**, 1064 (1916).

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

The Reaction between Quinones and Sodium Enolates. VII. Bromopseudocumoquinone and Sodium Malonic Ester[1]

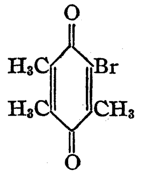
BY LEE IRVIN SMITH AND KENNETH C. JOHNSON[2]

So far, in the work described in this series of papers, two types of quinones have been investigated: (a) completely methylated para benzoquinones, represented by duroquinone[3] and by 2,3-dimethylnaphthoquinone[4]; (b) a quinone with one free position, pseudocumoquinone.[5] In the reactions with sodium enolates, such as sodium malonic ester, quinones of type (a) have behaved as pentad-enol systems and have given coumarin derivatives, while the quinone of type (b) reacted through the conjugated system terminating in the free position, and gave benzofuran derivatives. At the beginning of this work, duroquinone was selected for investigation because a fully substituted quinone, containing no *replaceable* group, was desired in order that the reaction might be with certainty confined to an addition.

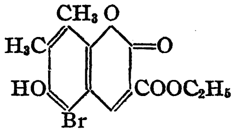
A great variety of active methylene compounds has been used in reactions with halogenated quinones, such as 2,3-dichloro-α-naphthoquinone.[6] In general, one or both of the halogen atoms were replaced, but when only one halogen atom was present this might or might not react, and the reaction has involved the replacement even of an ether group by a malonic ester residue although halogen was available.[7] Moreover, the halogen in 2-bromo-3-mesityl-α-naphthoquinone was inert toward sodium malonic ester.[8]

The mononuclear halogenated quinones also have shown the same irregularities. Chloranil[6a,9] reacted with replacement of two (para) chlorine atoms by malonic ester residues; in the diethers of chloroanilic acid both ether groups were replaced;[10] and in dibromothymoquinone only one halogen (ortho to the methyl group) was replaced by the malonic ester residue, while with aniline, the *methyl group* was replaced by the anilino group.[11]

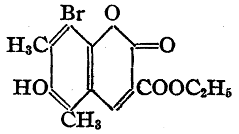
Because of the variety of the reactions shown by halogenated quinones, it was of interest to examine the behavior of bromopseudocumoquinone (I) toward sodium malonic ester. This quinone could react by replacement of the halogen by the malonic ester residue and it also offered the possibility of a reaction of the type (a) quinones already studied which would involve a methyl group and lead to a coumarin derivative. In the latter case, three different coumarins (A, B, C) could result, since the three methyl groups in the quinone were not equivalent (*o*-, *m*- or *p*- to the bromine atom). If only one of the methyl groups were involved, it was hoped that a study of the reaction would yield information concerning the activating effects of the groups upon each other as transmitted through the quinone ring.



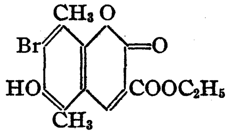
I



A (ortho)



B (meta)
III



C (para)

When bromopseudocumoquinone (I) was added to a solution of sodium malonic ester in absolute alcohol, there resulted a red sodium derivative (II) which, when decomposed by hydrochloric acid, gave a golden-yellow substance (III). Analysis and determination of the molecular weight showed this substance to have the composition $C_{14}H_{13}O_5Br$. The equation which Smith

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[1] Part VI, THIS JOURNAL, **59**, 667 (1937).

[2] Abstracted from a thesis by Kenneth Carl Johnson presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, March, 1937.

[3] (a) Smith and Dobrovolny, THIS JOURNAL, **48**, 1693 (1926); (b) Smith and Tenenbaum, *ibid.*, **59**, 667 (1937).

[4] Smith and Webster, *ibid.*, **59**, 662 (1937).

[5] Smith and MacMullen, *ibid.*, **58**, 629 (1936).

[6] Liebermann, (a) *Ber.*, **31**, 2903 (1898); (b) *ibid.*, **32**, 916 (1899); (c) *ibid.*, **33**, 566 (1900); (d) Michel, *ibid.*, **33**, 2402 (1900); (e) Hirsch, *ibid.*, **33**, 2412 (1900).

[7] Liebermann, *ibid.*, **32**, 260 (1899).

[8] Han Chiang Yuan, *J. Chinese Chem. Soc.*, **3**, 141 (1935); from *C. A.*, **29**, 6229 (1935).

[9] Stieglitz, *Am. Chem. J.*, **13**, 38 (1891).

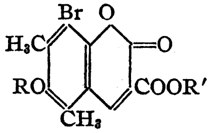
[10] (a) Grindley and Jackson, *Ber.*, **26**, 397 (1893); (b) *Am. Chem. J.*, **17**, 579, 633 (1895); (c) Jackson and Oenslager, *ibid.*, **18**, 1 (1896); (d) Bentley, *ibid.*, **20**, 472 (1898).

[11] Hoffmann, *Ber.*, **34**, 1558 (1901).

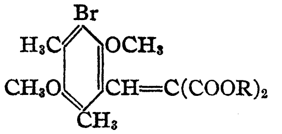
and Dobrovolny[3a] found to hold for the reaction between duroquinone and malonic ester, when applied to I, would lead to a product having the composition of III.

$$\underset{\text{I}}{2C_9H_9O_2Br} + C_7H_{12}O_4 \longrightarrow \underset{\text{III}}{C_{14}H_{13}O_5Br} + C_2H_5OH + C_9H_{11}O_2Br$$

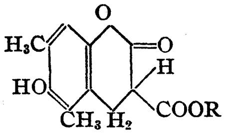
It was obvious at the outset, therefore, that the bromine atom in the quinone I had not reacted, but that one of the methyl groups had been involved and that the product III was undoubtedly one of the coumarin esters A, B and C. The substance III was an ester, for it could be hydrolyzed to an acid (IV). The yellow ester III also contained one hydroxyl group for it could be converted into a white monoacetate (V); likewise the yellow acid IV could be converted into a white monoacetate (VI). Only a single product (VII) could be obtained by methylation of the ester III with methyl sulfate and alcoholic potassium hydroxide, and the same methyl derivative VII was obtained from the acid IV, or from the acetates V and VI. The composition of this methyl derivative was $C_{13}H_{11}O_5Br$—hence the ester grouping in III was hydrolyzed during the methylation, and VII was a monomethyl derivative of IV. Catalytic reduction of the ester III gave a colorless product (VIII) $C_{14}H_{16}O_5$, which contained no bromine. This composition corresponded to that required by reduction of one double bond, and replacement of the bromine by hydrogen, in the ester III.



III, R = H, R' = C_2H_5
IV, R = H, R' = H
V, R = Ac, R' = C_2H_5
VI, R = Ac, R' = H
VII, R = CH_3, R' = H



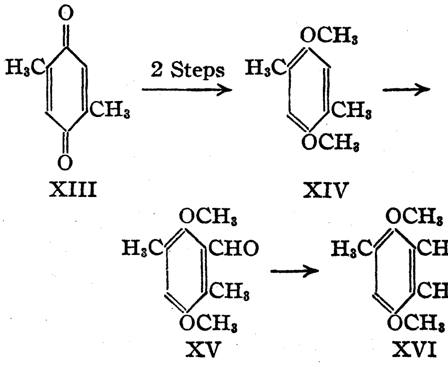
D, R = C_2H_5
E, R = H



VIII, R = C_2H_5
VIIIa, R = H

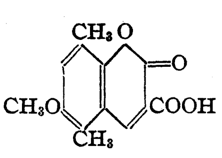
It was planned to open the coumarin ring by methylation and so obtain the ester D or the acid E which could then be synthesized or degraded to simpler compounds, analogous to the method used by Smith and Dobrovolny[3a] in handling the product from duroquinone. But the replacement of a methyl group by bromine in position 8 of the coumarin rendered the hetero ring surprisingly resistant to opening, and it was not possible to obtain any product other than VII by any of the methods tried.

Since it was not possible to degrade the ester III to any simpler compound, it became necessary to synthesize either the ester III or one of its derivatives. At this point nothing about the chemistry of III or its derivatives was known which would point to a choice among the possible structures A, B and C for III, consequently the choice of which of these to synthesize first was governed by the accessibility of the starting materials. Of the three xyloquinones which constituted the starting points for the respective series, the para isomer was most readily obtained; hence the first attempt was directed toward a synthesis of C. *p*-Xyloquinone (XIII) was converted to 1,4-dimethyl-2,5-dimethoxybenzene (XIV) and the latter was converted to 2,5-dimethyl-3,6-dimethoxybenzaldehyde (XV). The aldehyde was difficult to brominate, and when subjected to rather vigorous conditions it gave a product which could not be purified. It was therefore condensed with malonic acid to give the benzalmalonic acid XVI and this, when heated above its melting point, lost methyl alcohol to give 3-carboxy-6-methoxy-5,8-dimethylcoumarin XVII.[3a]

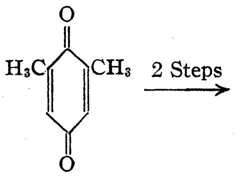


XIII XIV
XV XVI

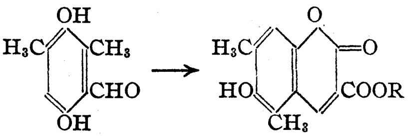
Bromination of XVII to give C was unsuccessful; the product showed only a slight test for halogen and even after several recrystallizations melted over a wide range. But the melting point of XVII, 230°, was 20° higher than that of the bromocoumarin VII, and since all previous experience with these compounds had shown that the introduction of a bromine atom into the ring raised the melting point considerably, it appeared



XVII



XVIII



XIX

XX R = H
XXI R = C_2H_5

quite certain that the ester III did not belong in the para series (C).

At this point, attention was turned to the meta series and hence to a synthesis of B or some compound derived from it.[12] *m*-Xyloquinone XVIII was prepared by oxidation of mesidine, and by a series of reactions similar to that outlined above the quinone was converted into 2,4-dimethyl-3,6-dihydroxybenzaldehyde (XIX). Condensation of XIX with malonic acid gave 3-carboxy-6-hydroxy-5,7-dimethylcoumarin, (XX). Malonic ester did not condense well with the aldehyde XIX, but the ethyl ester XXI was easily prepared from the acid XX. Bromination of the coumarin acid XX to the bromocoumarin IV was unsuccessful, but when the ethyl ester XXI was catalytically reduced, a dihydro ester resulted which was identical in all respects with the ester VIII prepared by reduction of III. A specimen of VIII prepared by reduction of I gave, when oxidized with ferric chloride, a coumarin acid identical in all respects with the acid XX.

The substance III obtained from the reaction between bromopseudocumoquinone and sodium malonic ester therefore possesses the structure B and is 3-carbethoxy-6-hydroxy-5,7-dimethyl-8-bromocoumarin. In this reaction the bromine atom of the quinone is unaffected; the quinone behaves as a pentad–enol system and it is the methyl group meta to the bromine which is involved in the reaction. It is proposed to explore the limits of this reaction in a series of brominated alkyl quinones and to discover how far this inertness of the bromine atom extends.

Although the initial experiments on the reaction between the quinone and sodium malonic ester were carried out in alcohol, the yield of product III by this procedure was very low and it was possible to account for but a small fraction of the quinone used. This was due to the action of sodium ethoxide which rather rapidly converted the quinone to tarry products. When the red sodium compound (II) was prepared in benzene, according to the original procedure of Smith and Dobrovolny,[3a] the ester III obtained from it was accompanied by large amounts of a highly fluorescent viscous oil, and the yield of III was low. Better results were obtained when the quinone was added to a suspension of sodium malonic ester (free from alcohol) in ether, but it was possible to account for only about 30% of the starting quinone when this procedure was used. When, however, the quinone was added to an alcoholic solution of malonic ester in which finely divided magnesium ethoxide was suspended, a reddish solid soon precipitated with very little tarry by-product. This magnesium compound (IX) when filtered and dried was light tan in color. Dilute acids readily converted it to the ester III and with dilute hydrochloric acid the reaction was quite vigorous. The yield of coumarin ester III when prepared in this way was approximately the theoretical assuming two moles of quinone necessary to form one mole of III. The alcoholic filtrate from the magnesium compound yielded the fairly stable, brilliant black quinhydrone of I. Practically all of the quinone used was accounted for by ester III and quinhydrone recovered.

While the discovery that this magnesium derivative was readily formed and that it could be

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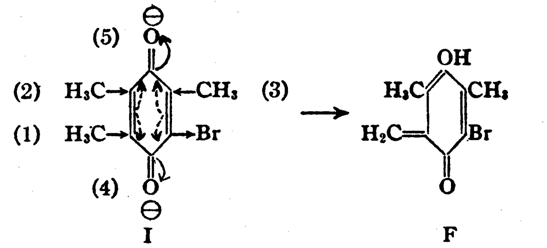
[12] While this synthesis was in progress, Dr. I. M. Webster and Mr. T. A. Geissman of this Laboratory called the attention of the authors to the fact that an application of the electronic principles used extensively by the English School of Organic Chemists [see C. K. Ingold, *Chem. Rev.*, **15**, 225 (1934)] would lead to the prediction that B was the correct structure for III.

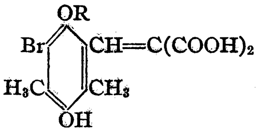


I F

In the quinone I, the electrons tend to shift as shown by the arrows. One-half of the molecule is symmetrical, so that the effects of the methyl groups 1 and 2 are the same. But in the other half of the molecule, the bromine atom has a strong electron affinity and this counteracts the tendency for the electrons to shift to the oxygen atom 4, while the methyl group 3 augments the tendency for the electrons to shift to the oxygen atom (5). As a result of these effects, oxygen atom 5 is more electronegative than 4. Consequently, when enolization occurs in the pentad–enol system, the hydrogen would shift to the more negative oxygen atom (5); and the enol would have structure F in which the methyl group (1) meta to the bromine atom, is part of the new conjugated system.

converted to III in good yield was of great practical value in these researches, the most interesting and significant property of the substance was the fact that it could be converted into a series of derivatives closely related to, but different from the series of derivatives obtained from the ester III or from the sodium compound II. When the magnesium compound (IX) was decomposed by freshly distilled methyl sulfate in methanol, a *yellow* product (X) melting at 240° was obtained. Analysis of this product X showed a composition closely approximating $C_{13}H_{16}O_6Br$, and it contained one methoxyl group. The substance was unaffected by boiling it in acetone solution with hydrochloric acid, but hydrobromic acid in acetic acid converted it to the coumarin acid IV. The action of acetic anhydride converted X into a colorless acetyl derivative (XII), which was different from any acetate obtained from the ester III or from its derivatives. Methylation of X by methyl sulfate and alkali gave the same methyl ether VII as was obtained by methylation of III. When the magnesium compound IX was subjected to the action of acetyl chloride (distilled from dimethylaniline directly onto the substance) it gave an oily reaction product from which yellow, solid acetyl derivative (XI) was finally isolated.

When methylated, the acetyl derivative XI gave the methyl ether VII; hydrolysis of XI by acetone–hydrochloric acid gave the coumarin acid IV. Because of the formation of a series of products entirely different from those obtained from the coumarins III and IV, it is believed that these substances are derived from the primary metallic derivative formed by 1,4-addition to the conjugated system in F. While much more work remains to be done on this series of compounds, the methyl ether X and the acetate XI are provisionally given the structures shown.[13]



X R = CH_3
XI R = Ac

Experimental Part[13a]

Synthesis of the Quinone I. 5-Bromo-3,6-dinitropseudocumene.—A solution of 5-bromopseudocumene (50 g.) in chloroform (200 cc.) was floated on to sulfuric acid (200 cc.). Fuming nitric acid (50 g., d. 1.5) was added dropwise (forty-five minutes) with cooling (−5 to 0°) and stirring. The initial dark color gradually lightened and a solid began to separate. Stirring was continued for thirty minutes after adding the nitric acid; this was followed by stirring for thirty minutes at room temperature. The reaction mixture was a thick emulsion, which did not separate well into layers, but the layers were separated as completely as possible and the acid was extracted once or twice with fresh chloroform. The oil and the chloroform solutions were combined, washed with water, dilute alkali and again with water. Ethanol (300 cc.) was added and the solution concentrated to half its volume. The mixture was cooled to 0°, and the solid was removed, washed with cold alcohol and dried. The white product weighed 61 g. (84%) and melted at 216–217°. When crystallized twice from chloroform–ethanol, the substance melted at 221–222°.[14] From the filtrates about 6 g. more was obtained, bringing the total yield to 93%. The substance could be recrystallized from benzene–alcohol or chloroform–alcohol, but the reaction product, isolated as described, was quite pure.

Anal. Calcd. for $C_9H_9O_4N_2Br$: C, 37.37; H, 3.14; Br, 27.6. Found: C, 37.38; H, 3.16; Br, 27.8.

The stannichloride of 5-bromo-3,6-diaminopseudocumene was obtained when a hot solution of stannous chloride (350 g.) in hydrochloric acid (400 cc.) was added quickly to a hot solution of the bromonitro compound (53 g.) in acetic acid (400 cc.). The reaction was vigorous and it was necessary to use a large flask (5 liters). The reaction mixture was cooled to 0°, the solid filtered and washed with alcohol (80 cc.) and ether (60 cc.). The product was contaminated with tin salts; it weighed 85 g. (theory 73 g.).[15]

The amine was isolated by extracting with ether a suspension of the stannichloride in alkali. Crystallized from alcohol, it was almost white (darkened at 150°) and melted at 155° to a black liquid.

Anal. Calcd. for $C_9H_{13}N_2Br$: C, 47.16; H, 5.72; Br, 34.9. Found: C, 47.07; H, 5.59; Br, 35.3.

The stannichloride (58 g.) was added to a solution of ferric chloride (275 g.) in water (275 cc.) and hydrochloric acid (25 cc.) in a flask equipped for steam distillation. After standing at room temperature for thirty minutes, the mixture was warmed on the steam-bath for thirty minutes and then steam distilled. The quinone I, isolated from the distillate, weighed 26 g. (82% based on the dinitro compound taken) and melted at 79–80°. It could be crystallized from alcohol in golden-yellow needles, but the crude product was sufficiently pure for most purposes.

Anal. Calcd. for $C_9H_9O_2Br$: C, 47.16; H, 3.97; Br, 34.9. Found: C, 47.43; H, 4.02; Br, 34.9.

When the quinone (0.2 g.) in alcohol (25 cc.) was added to the hydroquinone (0.2 g.) in alcohol (50 cc.) and the yellow solution concentrated on the steam-bath until the color darkened, there resulted the black, stable quinhydrone melting at 148.5–149.5°.

Bromopseudocumohydroquinone.—To the quinone (1 g.) suspended in alcohol (5 cc.) was added a solution of stannous chloride (2 g.) in dilute hydrochloric acid (25

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(13) Farmer, Ghosal and Kon [*J. Chem. Soc.*, 1804 (1936)] have recently obtained two types of metallic derivatives by the addition of sodium malonic esters to α-β acetylenic esters. These two types of metallic derivatives are closely related, but each gives its own series of alkyl derivatives.

(13a) Microanalyses by J. W. Opie.

(14) Fittig [*Ann.*, 147, 14 (1868)] reports the m. p. as 214–215°.

(15) Nietzki and Schneider, *Ber.*, 27, 1428 (1894).

cc.). The mixture was warmed until the color disappeared, and the product appeared on cooling. Crystallized from dilute alcohol containing a little stannous chloride and hydrochloric acid, the product formed white needles (0.9 g.), darkened at 170° and melted at 185° (dec.).

The dimethyl ether resulted when the hydroquinone (0.5 g.) in methanol (5 cc.) and methyl sulfate (3 cc.) was warmed and treated with small portions of saturated potassium hydroxide in methanol until the reaction mixture was strongly alkaline. The solution was acidified, the solid was removed and crystallized from methanol. The yield of white product, melting at 71–72°, was nearly quantitative.

Anal. Calcd. for $C_{11}H_{15}O_2Br$: C, 50.97; H, 5.83; Br, 30.9. Found: C, 51.79; H, 6.04; Br, 30.8.

The diacetate, prepared in the usual way, and crystallized from alcohol, formed white needles which melted at 178–179°.

Anal. Calcd. for $C_{13}H_{15}O_4Br$: C, 49.52; H, 4.79; Br, 25.4. Found: C, 49.92; H, 4.92; Br, 25.4.

The dibenzoate, prepared by the Schotten–Baumann method and crystallized from chloroform–alcohol, was white and melted at 253–255°.

Anal. Calcd. for $C_{23}H_{19}O_4Br$: C, 62.87; H, 4.37; Br, 18.2. Found: C, 63.28; H, 4.56; Br, 18.1.

Addition of Malonic Ester to the Quinone I. (a) In Alcohol.—A solution of the quinone (11.5 g.) in dry alcohol (100 cc.) was added dropwise to a solution of malonic ester (8 g.) and sodium ethoxide in dry alcohol (1.5 g. sodium, 50 cc. alcohol). The color became bluish-violet at once, then changed to red and a dark solid began to separate within ten minutes. After standing for thirty minutes the solution was poured onto ice (500 g.) and hydrochloric acid (50 cc.). The precipitate gradually collected together into a dark spongy mass which solidified on standing overnight. The dark solid was dissolved in hot alcohol and the solution was filtered. The cooled filtrate deposited 2 g. (25%) of **3-carbethoxy-6-hydroxy-5,7-dimethyl-8-bromocoumarin** (III) in the form of dark yellow needles melting at 200°. The rest of the reaction product was a dark oil from which no other solids could be isolated.

Anal. Calcd. for $C_{14}H_{13}O_5Br$: C, 49.26; H, 3.84. Found: C, 48.93; H, 4.26.

(b) In Ether.—Sodium (0.5 g.) was dissolved in dry alcohol (10 cc.) and after ethyl malonate (3.5 g.) was added the solvent was removed under reduced pressure. The residual white powder was suspended in ether (150 cc.) and a solution of quinone I (1 g.) in ether was added. After refluxing on the steam-bath for twelve hours, the red sodium compound (II) was filtered, washed with ether and dried. Decomposition of the sodium compound with acids gave III melting at 200° in about 25% yield and from the ethereal filtrates some quinone could be recovered.

(c) In Benzene.—The procedure of Smith and Dobrovolny[3a] was followed, but the yield of III was very low. Apparently the prolonged heating (eight days) in the presence of alkali largely destroyed both the quinone and the product.

(d) Using Magnesium Malonic Ester.—Magnesium ethoxide (6 g., freshly pulverized) was refluxed with malonic ester (6 g.) and dry alcohol (250 cc.). The quinone I (8 g.) in alcohol was added dropwise while a current of air was bubbled through the reaction mixture. Refluxing was continued, with air passing through, for twelve hours longer. The tan solid IX was filtered and washed with ether; the first crop of material weighed 10.8 g., and from the filtrate and washings 1.6 g. more was obtained. The substance was contaminated with magnesium ethoxide and it was not analyzed. When decomposed by hydrochloric acid the magnesium compound IX (1 g.) gave slightly more than 0.4 g. of the coumarin III melting at 200°. The ether filtrates when evaporated gave a dark oil consisting of malonic ester and quinhydrone.

3 - Carbethoxy - 6 - acetoxy - 5,7 - dimethyl - 8 - bromocoumarin (V).—The ester III (1 g.) was boiled with acetic anhydride (20 cc.) and sulfuric acid (5 drops). After thirty minutes the solution was poured into water and the mixture made alkaline with ammonia. The solid was dissolved in chloroform, the solution filtered, alcohol added and the filtrate and the solvents evaporated to a small volume. The solid was removed and recrystallized from alcohol. It was white, weighed 0.9 g. (88%) and melted at 160–161°.

Anal. Calcd. for $C_{16}H_{15}O_6Br$: C, 50.13; H, 3.95. Found: C, 50.36; H, 4.15.

3 - Carboxy - 6 - hydroxy - 5,7 - dimethyl - 8 - bromocoumarin (IV).—The ester III (0.5 g.) was dissolved in acetone (25 cc.) and refluxed for three hours with hydrochloric acid (25 cc.) and water (25 cc.). The hot solution was filtered and the filtrate on cooling deposited a yellow solid. Crystallized from benzene, the substance weighed 0.3 g. (65%) and formed bright yellow needles melting at 250°.

Anal. Calcd. for $C_{12}H_9O_5Br$: C, 46.00; H, 2.90. Found: C, 46.41; H, 2.99.

3 - Carboxy - 6 - acetoxy - 5,7 - dimethyl - 8 - bromocoumarin (VI).—Acetylation of the acid IV gave white cottony needles of VI melting at 223°.

Anal. Calcd. for $C_{14}H_{11}O_6Br$: C, 48.32; H, 3.12. Found: C, 48.35; H, 3.29.

3 - Carboxy - 6 - methoxy - 5,7 - dimethyl - 8 - bromocoumarin (VII).—To the ester III (0.5 g.) in boiling methanol (10 cc.) and methyl sulfate (4 g.) was added dropwise an excess of a saturated solution of potassium hydroxide in methanol. The reaction mixture was diluted with water, acidified with hydrochloric acid, and extracted with ether. Evaporation of the ether left a yellow oil which solidified when rubbed with cold methanol. The product, crystallized from methanol, was almost white. It weighed 0.1 g. and melted at 210°. Methylation of the acid IV or the acetate V also gave VII.

Anal. Calcd. for $C_{13}H_{11}O_5Br$: C, 47.71; H, 3.40; OCH_3, 9.5. Found: C, 47.98; H, 3.63; OCH_3, 9.4.

3 - Carbethoxy - 6 - hydroxy - 5,7 - dimethyl - 3,4 - dihydrocoumarin (VIII).—The ester III (0.2 g.) was dissolved in ethanol (100 cc.) and a palladium catalyst[16] (0.2 g.) was added, and the mixture was shaken for two hours under hydrogen at 42 pounds (2.8 atm.) pressure. The catalyst was removed, the filtrate concentrated under

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[16] Busch and Stöve, *Ber.*, **49**, 1064 (1916).

reduced pressure and then diluted with water until precipitation started. After standing in the icebox for two hours, the solid was removed and recrystallized from dilute ethanol. The substance formed silvery white needles melting at 142–143°.

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.61; H, 6.06. Found: C, 63.31; H, 5.75.

Synthesis of XVII from *p*-Xyloquinone (XIII).—*p*-Xyloquinone (XIII) was prepared in 40% yield by oxidation of pseudocumidine-5 by chromic acid. It was isolated by steam distillation from the reaction mixture. The melting point was 124–125°.[17] Reduction of the quinone by stannous chloride and hydrochloric acid in aqueous alcohol gave the **hydroquinone** in nearly quantitative yield. Crystallized from water, the white needles melted at 215–216°.[18]

1,4-Dimethyl-2,5-dimethoxybenzene (XIV) was obtained in good yield by methylating the hydroquinone in methanol with methyl sulfate and methyl alcoholic potassium hydroxide. The product, steam distilled and crystallized from methanol, melted at 110–111°.[19]

2,5-Dimethyl-3,6-dimethoxybenzaldehyde (XV).—The dimethyl ether XIV (3.1 g.) was dissolved in benzene (200 cc.). Zinc cyanide[20] (4.5 g.) was added, the mixture was strongly cooled and dry hydrogen chloride was passed in with stirring for four hours. At this point aluminum chloride (5 g.) was added, and hydrogen chloride again passed in for eight hours. The temperature was then allowed to rise to 25° and the gas was passed in for twelve hours longer. The reaction mixture was then kept at 60° for eight hours, then allowed to stand overnight at room temperature. The benzene was decanted and the oily solid washed with dry benzene. Dilute hydrochloric acid was added and the mixture was steam distilled. The waxy solid in the distillate was crystallized from dilute methanol. The aldehyde (3 g., 83%) formed yellow needles melting at 59–60°. It could be purified by dissolving it in bisulfite, filtering off any insoluble material and acidifying the filtrate.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 67.99; H, 7.27. Found: C, 67.57; H, 7.09.

The oxime, prepared in the usual way and crystallized from dilute alcohol, formed white needles melting at 118–119°.

Anal. Calcd. for $C_{11}H_{15}O_3N$: C, 63.12; H, 7.23. Found: C, 63.35; H, 7.23.

2,5 - Dimethyl - 3,6 - dimethoxybenzalmalonic Acid (XVI).—The aldehyde XV (1 g.) and malonic acid (0.6 g.) were dissolved in methanol (10 cc.) and piperidine (0.6 g.) was added. After warming for four days at 65°, the reaction mixture was acidified with dilute hydrochloric acid and the solid was removed and crystallized from dilute methanol. It formed white needles, melting at 195° with evolution of a gas and the melt, on cooling, solidified to a bright yellow solid which remelted at about 215° (XVII).

Anal. Calcd. for $C_{14}H_{16}O_6$: C, 59.97; H, 5.76. Found: C, 59.67; H, 5.60.

3 - Carboxy - 6 - methoxy - 5,8 - dimethylcoumarin (XVII).—The coumarin was obtained by fusion of the acid XVI, but it also resulted by prolonged heating of the aldehyde XV (0.1 g.) with malonic acid (0.1 g.) in ethanol (5 cc.) and piperidine. Each day for a period of four days, 3 drops of piperidine was added and the mixture was warmed on the steam-bath for six hours, then allowed to stand overnight. The deep yellow solution was acidified with hydrochloric acid, and the solid was removed and crystallized from dilute methanol. The yellow needles weighed 0.1 g. and melted at 229–230°.

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.88; H, 4.87. Found: C, 62.13; H, 4.81.

Synthesis of XX from *m*-Xyloquinone (XVIII).—The quinone XVIII was prepared by oxidation of mesidine[21] in dilute sulfuric acid by chromic acid.[17] The quinone was isolated by steam distillation and ether extraction of the distillate. Crystallized from dilute methanol it formed light orange needles melting at 74–75°. The yield was 40%. Reduced by stannous chloride in hydrochloric acid, the quinone (1 g.) was converted to the hydroquinone (0.9 g.) which, after crystallization from water, melted at 147–148°.[17]

2,4 - Dimethyl - 3,6 - dihydroxybenzaldehyde (XIX).—The aldehyde group was introduced into the hydroquinone by the same procedure as that used for the preparation of the aldehyde XV. The aldehyde, crystallized from dilute methanol, was yellow and melted at 145°. It was soluble in bisulfite solution.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.09; H, 6.07. Found: C, 65.35; H, 5.93.

3 - Carboxy - 6 - hydroxy - 5,7 - dimethylcoumarin (XX).—The aldehyde XIX (0.1 g.) and malonic acid (0.1 g.) were dissolved in ethanol (5 cc.). Piperidine (3 drops) was added and the mixture was allowed to stand for three days at room temperature. The deep red solution was acidified with dilute hydrochloric acid, precipitating a yellow solid. Crystallized from dilute methanol, this weighed 0.15 g. and melted at 235–236°.

Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.90; H, 4.43.

3 - Carbethoxy - 6 - hydroxy - 5,7 - dimethylcoumarin (XXI).—The coumarin acid XX (0.1 g.) was esterified by refluxing it with dry ethanol (100 cc.) and sulfuric acid (5 drops) for three days. Crystallized from dilute ethanol, the substance melted at 165–166°.

Anal. Calcd. for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.11; H, 5.33.

When hydrolyzed by boiling acetone–hydrochloric acid, the ester XXI gave the acid XX.

3 - Carbethoxy - 6 - hydroxy - 5,7 - dimethyl - 3,4 - dihydrocoumarin (VIII).—When the ester XXI was reduced catalytically using the palladium catalyst, the product was the ester VIII, melting point and mixed melting point 140–143°. Specimens of the ester VIII prepared by two methods gave on oxidation with ferric chloride the coumarin acid XX, melting point and mixed melting point 233°.

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[17] Nölting and Baumann [*Ber.*, **18**, 1151, 2667 (1885)] reported the melting point as 123–124°.

[18] Conant and Fieser, This Journal, **45**, 2194, 3348 (1923).

[19] Nölting [*Ber.*, **23**, 3251 (1890)] reported the melting point as 108°.

[20] Adams and Levine, This Journal, **45**, 2373 (1923).

[21] The mesidine used for this preparation was prepared by A. C. Keyl from bromomesitylene.

Derivatives of the Magnesium Compound (IX).—The magnesium derivative IX (2 g.) was heated with methanol (20 cc.) and methyl sulfate (5 g.). The hot solution was filtered and the dark yellow filtrate, on cooling, deposited fine yellow needles. Crystallized from acetic acid, the product (X) weighed 0.9 g. and melted at 240–241°.

Anal. Calcd. for $C_{13}H_{13}O_6Br$: C, 45.22; H, 3.80; OCH_3, 9.0. Found: C, 45.75; H, 3.90; OCH_3, 9.7.

The substance X was unchanged after refluxing for three hours with acetone–hydrochloric acid, but when refluxed with acetic acid (15 cc.) and hydrobromic acid (5 cc., 40%), X gave the coumarin acid IV, melting point and mixed melting point 250°. Acetylation of X by warming it with acetic anhydride and a drop of sulfuric acid gave a white substance (XII) which melted at 187–188° after crystallization first from dilute acetic acid and then from methanol. The substance was analyzed but the analysis did not correspond to that required for any simple acetyl derivative of IX.

The yellow acetyl derivative XI resulted when the magnesium compound IX (1 g.) was warmed with pure acetyl chloride (freshly distilled from dimethylaniline). Crystallized from acetic acid, the product formed yellow needles which melted at 231–232°.

Anal. Calcd. for $C_{14}H_{13}O_7Br$: C, 45.04; H, 3.50. Found: C, 45.08; H, 3.87.

When the yellow acetyl derivative XI was methylated by methyl sulfate and methyl alcoholic potassium hydroxide, the product was the methyl derivative VII, melting point and mixed melting point 210°.

Summary

1. Sodium and magnesium ethoxides have been used as condensing agents for the addition of malonic ester to bromopseudocumoquinone leading to the formation of a sodium and a magnesium derivative, respectively.

2. Both metallic derivatives were converted by acids to the same substance, 3-carbethoxy-6-hydroxy-5,7-dimethyl-8-bromocoumarin (III), the structure of which was proved by conversion to the bromine-free coumarin acid (XX) and synthesis of the latter from *m*-xyloquinone.

3. The chemical properties of the coumarin ester III and many of its derivatives have been described.

4. In the reaction with the enolates of malonic ester, the bromine atom of the bromoquinone was unaffected. The quinone behaved as a pentadenol system, the methyl group meta to the bromine atom reacting.

5. The magnesium compound gave rise to two series of derivatives: one identical with the series of derivatives obtained from the sodium compound and the other closely related to, but different from, this series.

6. Starting with *p*-xyloquinone, 3-carboxy-6-methoxy-5,8-dimethylcoumarin (XVII) was synthesized.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 15, 1937

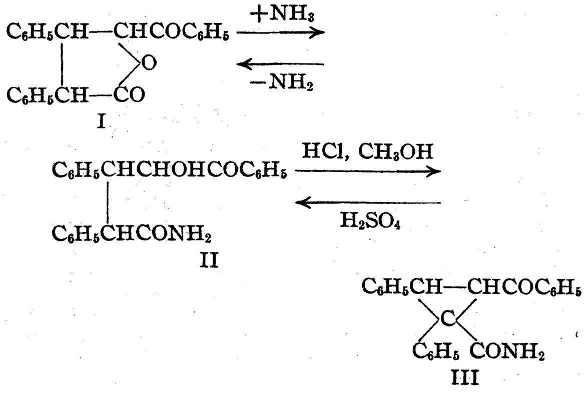
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

The Action of Alkaline Reagents on Diphenylbenzoylbutyrolactone

BY C. F. H. ALLEN, E. E. MASSEY[1] AND R. V. V. NICHOLLS

The γ-lactone ring is usually opened by alkaline reagents with the consequent formation of a salt of a γ-hydroxy acid; upon acidification an equilibrium mixture is formed, which is usually preponderantly in the lactone form. This behavior is exhibited by α,β-diphenyl-γ-benzoylbutyrolactone I, but if the alkaline solution is not acidified immediately it becomes yellow and deposits a mixture of solids and oil when treated with acids. The new substances are obviously secondary products resulting from the action of alkalies on the highly substituted salt obtained on ring opening. The nature of these products varies to some extent with the reagent used, and hence it is convenient to describe separately the action of each basic substance.

The lactone is insoluble in ammonium hydroxide but gradually dissolves in alcoholic ammonia to give a substance, the properties of which are in best agreement with the open chain hydroxy amide structure II. Thus, analysis shows that



I

II

III

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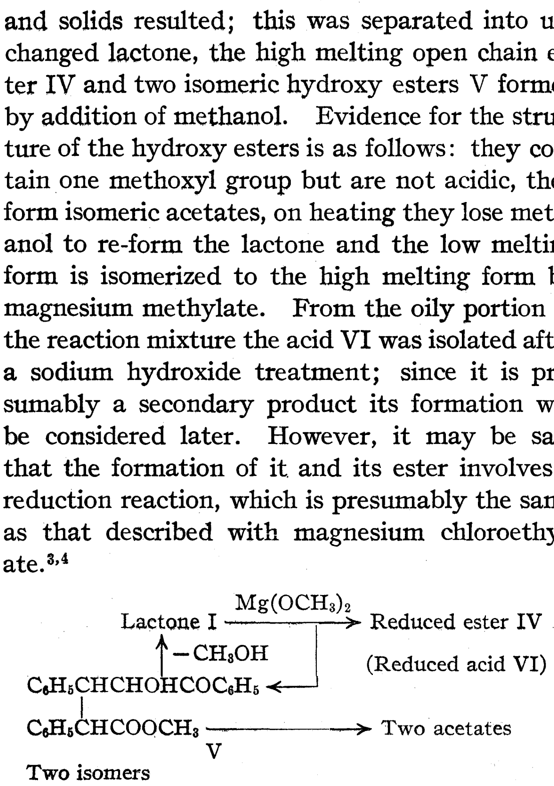
[1] Acknowledgment is hereby made of a bursary granted for one year by the National Research Council of Canada.

one ammonia has added; recrystallization from glacial acetic acid removes this and re-forms the lactone, while treatment with hydrogen chloride in methanol dehydrates it to the known cyclopropane amide III.[2] The direction of the latter reaction is reversed by concentrated sulfuric acid.

When alcoholic magnesium methylate was allowed to react with the lactone a mixture of oil and solids resulted; this was separated into unchanged lactone, the high melting open chain ester IV and two isomeric hydroxy esters V formed by addition of methanol. Evidence for the structure of the hydroxy esters is as follows: they contain one methoxyl group but are not acidic, they form isomeric acetates, on heating they lose methanol to re-form the lactone and the low melting form is isomerized to the high melting form by magnesium methylate. From the oily portion of the reaction mixture the acid VI was isolated after a sodium hydroxide treatment; since it is presumably a secondary product its formation will be considered later. However, it may be said that the formation of it and its ester involves a reduction reaction, which is presumably the same as that described with magnesium chloroethylate.[3,4]



The action of sodium methylate, alcoholic potash or sodium hydroxide on the lactone was very drastic, and only products of secondary reactions could be identified. These were a cyclopentadienone VII, one isomeric form of the acid VI, diphenylmaleic anhydride, diphenylsuccinic acid, the lactone VIII, benzaldehyde, stilbene and acetophenone. With the exception of the diketone, these substances are the ones that would be expected, taking into account the known action of alkaline reagents on α-hydroxy ketones[5] and hydrolysis. Opening of the lactone ring gives the salt of a hydroxy acid IX; part of this is reduced to the sodium salt of acid VI, and a part isomerized to a δ-hydroxy-γ-ketone X. Hydrolysis of the latter and oxidation would account for the diphenylsuccinic acid. Dehydrogenation of X either before or after reduction would give the salt of the unsaturated acid XI; one of the hydrolysis products of the latter is diphenylmaleic acid. The unsaturated acid XI (not isolated), as will become evident, is the intermediate in a series of reactions between the unsaturated lactone and the diketone. The ease of formation of benzaldehyde by hydrolysis of the several members of this series renders its detection of no significance.

On acidification, the free acids would be expected, though anhydride or lactol formation may occur when the configuration is favorable. Thus, the unsaturated acid XI at once gives the lactol XII, which loses water to form the lactone VIII actually isolated.

When the lactone VIII is dissolved in sodium hydroxide and carefully acidified and manipulated, the lactol XII is separated easily, in spite of the ease with which it loses water.

Both the lactone and lactol were known previously though obtained in another way.[6] By heating in a sealed tube with ammonia the lactone was reported to give a hydroxy amide XIII and lactam XIV and this was confirmed, as was the reduction by hydrogen iodide to give the 1,2-diphenyl-3-benzylcrotolactone XVI. The latter was also obtained in this paper by the action of zinc and acetic acid. The action of alkalies on the lactone is intimately connected with the diketone VII and is considered below.

The principal product (35%), resulting from the action of sodium methylate on lactone I is the bright yellow unsaturated 1,3-diketone VII. Its deep purple alkaline solutions are hydrolyzed very slowly and the products, after acidification, are the lactone VIII, diphenylmaleic anhydride and benzaldehyde; the last two are formed from the lactone VIII on similar treatment. Further evidence that the lactone and diketone are easily intraconvertible in alkaline solution is given by the fact that the same hydroxy amide XIII and lactam XIV are obtained from both by use of ammonia in a sealed tube. Hence the carbon chain and location of phenyl groups must be unchanged. Reduction of the diketone by zinc dust or hydriodic acid gives α,β-diphenyl-γ-benzal-

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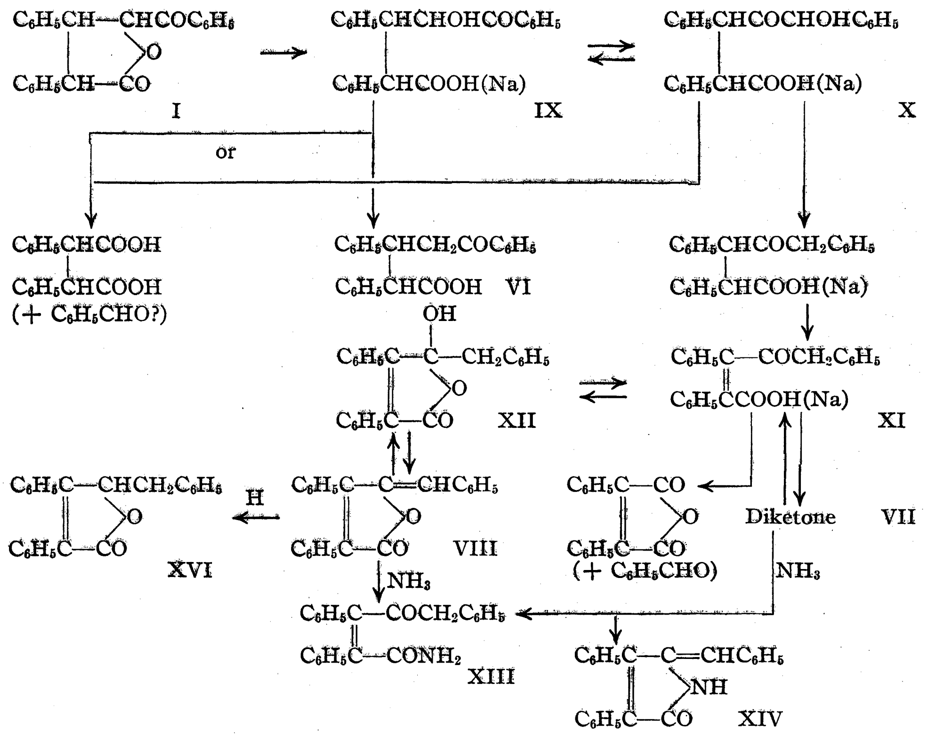
(2) Allen and Boyer, *Can. J. Research*, **9**, 159 (1933).

(3) Meerwein and Schmidt, *Ann.*, **444**, 221 (1935).

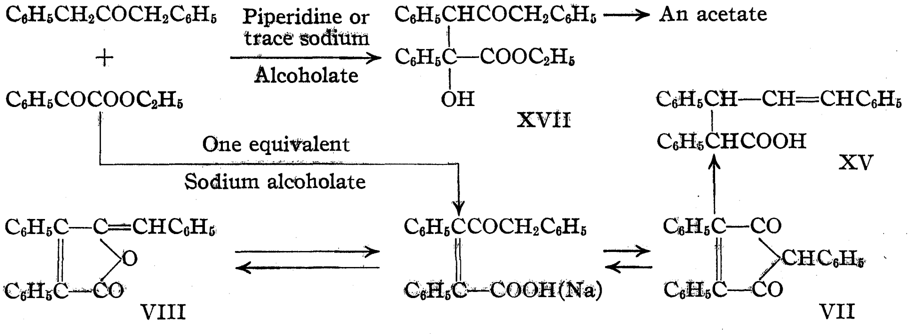
(4) It was important to know with certainty the structure of the hydroxy esters, since a single instance is recorded where a saturated lactone ring has been opened in the opposite way; butyrolactone and sodium ethylate give γ-ethoxybutyric acid and a dilactone. It may be a coincidence, but the b. p. of both γ-ethoxy- and γ-hydroxybutyric acids are the same, 231° [Fittig and Strom, *Ann.*, **267**, 191 (1892)].

(5) Kohler and Kimball, This Journal, **56**, 729 (1934); Kohler and Leers, *ibid.*, p. 981.

(6) Cohn, *Ber.*, **24**, 3961 (1891).



butyric acid XV, confirming the chain. It gives a mono-2,4-dinitrophenylhydrazone but does not form a quinoxaline. In the Grignard machine it shows one active hydrogen and gives slowly two additions. These reactions suggest the structure of a 1,3-diketone, and this was confirmed by a synthesis that also gave the unsaturated lactone VIII.



Dibenzyl ketone readily adds to benzoylformic ester in the presence of piperidine or a trace of sodium alcoholate at room temperature, but if the mixture is heated in the presence of an equivalent of alcoholate, water is eliminated and the product isolated depends on operating conditions; the use of sodium methylate favors the diketone, whereas with sodium ethylate the lactone or lactol XII (as sodium salt) separates during the heating, owing to insolubility. It cannot be said with certainty that the ester XVII is an intermediate product, because it is not converted into the other substances by sodium alcoholates.

The diketone is oxidized by permanganate to benzaldehyde, benzoic acid and carbon dioxide; chromic acid gives benzoic acid and a bimolecular product, while selenium dioxide forms the latter quantitatively. Though the diketone can be sublimed and is stable in air for a short time at the melting point, it is readily oxidized by atmospheric oxygen at this temperature to the bimolecular product. Mineral acids are without action at room temperature but destroy it at 100°. Hydrogen peroxide adds an atom of oxygen. The structure of the new derivative was not determined; it is altered by acetyl chloride, but the result is neither dehydration nor esterification. Other properties are recorded in the experimental part.

A comparison of the highly phenylated keto-hydroxy acid described in this paper with those previously known shows that the introduction of an additional phenyl has greatly increased the reactivity of the various groups. The most conspicuous differences are the facilitation of cleavage, the occurrence of dehydrogenation products and the tendency for the unsaturated lactone obtained to isomerize to a cyclic diketone. It is believed that the latter is the first representative of a new series.

Experimental

The bromination of a variety of δ-ketonic esters and the properties of the products has been well described[7] and there was no difficulty in adapting the procedure to the synthesis of methyl α,β-diphenyl-γ-benzoylbutyrate IV. The mixture of stereoisomers obtained by the addition of methyl phenylacetate to benzalacetophenone was used without separation, since all the bromo esters gave the lactone I as the principal product. The position of the bromine atom was thus made evident, the four monobromo substitution products being γ-bromo esters XVIII; their interrelation was shown by treatment with hydrogen bromide in acetic acid. Pyrolysis of the bromo esters gave the expected variety of substances. Thus, when methyl bromide was evolved[7a,c,8] the lactone resulted, but loss of hydrogen bromide[7,9] gave the reduced ester IV, the stereoisomeric acids VI, and a trace of what may be diketo acid.[10]

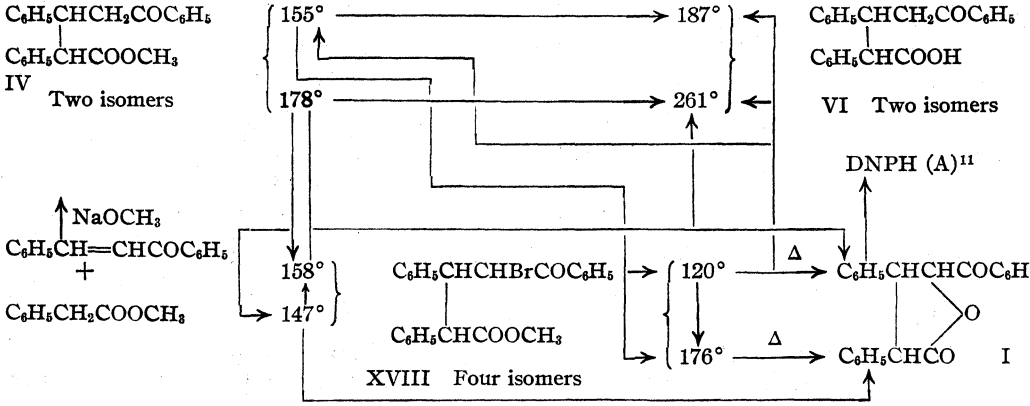
A. Preparation and Properties of the Lactone I.—1. Methyl α,β-diphenyl-γ-benzoylbutyrate IV was obtained by the addition of methyl phenylacetate[12] to benzalacetophenone in the presence of slightly over one equivalent of sodium methylate.[10] Since it was found unnecessary to use the separated bromo esters in a subsequent step, the mixture of esters, after recrystallization from benzene to remove some insoluble acid, was brominated directly. This gave four monobromo substitution products, m. p. 120, 147, 158 and 176°.

Seventy grams of the mixed keto ester was suspended in 400 cc. of carbon tetrachloride or glacial acetic acid, a few cc. of bromine added and the whole warmed in sunlight until the reaction commenced. Then the remainder of the bromine (total = 32 g.) was added slowly, during which time the suspended ester gradually dissolved. The thick, pasty solid that separated on cooling was filtered, washed and dried. The separation into the stereoisomeric forms involved a tedious fractionation, using ethyl acetate and methanol. The 176° isomer is isolated easily owing to its insolubility but the 158° isomer is the principal product; a constant melting (125°) mixture of the 158 and 147° isomers complicated the fractionation. When pure high melting ester (178°) was used, the yield of the 158° isomer was 60% if the bromination was done in acetic acid, but only 40% in carbon tetrachloride; this ester does not give the 176 or 120° forms.

The 176° form is sparingly soluble in all solvents; it separated in prisms from ethyl acetate. The other forms are moderately to very soluble in all solvents except petroleum ether. The 158° isomer separated from ethyl acetate in rods, and the other two from methanol as fine needles.

Anal. Calcd. for $C_{24}H_{21}O_3Br$: Br, 18.3. Found: (176°, 120°) 18.5; (158°) 18.2; (147°) 18.9.

One gram of each isomer in acetic acid was saturated with hydrogen bromide and worked up after three days. The 158 and 176° isomers were unchanged, but the 147° had completely isomerized to the 158° form and the 120°



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[7] (a) Kohler, *Am. Chem. J.*, **46**, 217, 474 (1911); (b) THIS JOURNAL, **39**, 1404, 1699, 2405 (1917); **41**, 683, 992 (1919); **44**, 840, 2536 (1922); (c) Hill, *ibid.*, **49**, 566 (1927).

[8] Kohler and his students, THIS JOURNAL, **41**, 683, 992, 1093 (1919); Hahn and Albee, *Am. Chem. J.*, **49**, 171 (1913). In the present instance, the loss of methyl bromide seems to take place even in boiling acetic acid; indeed, the best preparative method involved a short period of refluxing with potassium acetate.

[9] Haerdi and Thorpe, *J. Chem. Soc.*, **127**, 1237 (1925).

[10] The relation between the acids and esters is known from Avery's work, THIS JOURNAL, **52**, 3628 (1930).

[11] DNPH = 2,4-dinitrophenylhydrazone.

[12] We are grateful to Compagnie Parento Limited for the gift of a quantity of this ester.

to the 176° form. This is in agreement with the fact that only the 158 and 176° isomers are readily obtained.

The lactone I was most conveniently prepared from the mixed bromo esters by refluxing for two hours a mixture of 20 g. of the latter, an equal weight of potassium acetate and 100 cc. of glacial acetic acid; potassium bromide separated fairly rapidly. After pouring into water, the lactone was isolated by appropriate manipulations; the average yield of once recrystallized product was 65%. The filtrate contained considerable amounts of reddish oils and gums, with traces of lactone. The use of pyridine and dimethylaniline for an hour gave the same product but isolation was more laborious.

α,β-Diphenyl-γ-benzoylbutyrolactone is very soluble in benzene and chloroform, slightly soluble in the alcohols and ether, insoluble in petroleum ether, but moderately soluble in the other usual solvents. It is conveniently recrystallized from *n*-butanol or a chloroform–methanol mixture, from which it separates as rods, m. p. 157°.

Anal. Calcd. for $C_{24}H_{18}O_3$: C, 80.7; H, 5.0. Found: C, 80.8; H, 5.2.

A Zeisel determination was negative. In the Grignard machine it showed no active hydrogen, but gave two additions.

Pyrolysis of the pure bromo esters gave mixtures of products consisting of the reduced keto esters, the corresponding keto acids, the lactone and traces of what is probably a diketo acid. The 176° isomer gave the lactone nearly quantitatively; the methyl bromide (80% yield) evolved was collected in a freezing mixture. The diketo acid separated from methanol in long rods, m. p. 160°.

Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.1; H, 5.0. Found: C, 76.6, 76.7, 77.1; H, 4.4, 4.5, 4.3.

The phenylhydrazone (C; pale yellow cubes from ethanol m. p. 180°) and 2,4-dinitrophenylhydrazone (A; yellow prisms from methanol m. p. 210°) were prepared in the usual manner.

Anal. Calcd. for (A); $C_{29}H_{22}O_6N_4$: N, 10.7; for (C) $C_{29}H_{24}O_2N_2$: N, 6.5. Found: N; (A) 10.5; (C) 6.6.

2. **Reduction.**—The lactone was reduced by zinc and acetic acid to the low melting open-chain acid VI, but by hydrogen bromide to the high melting isomer. In the latter case the γ-bromoketo acid corresponding to the ester XVIII was presumably formed as an intermediate product; the reduction of α-bromo ketones by hydrogen bromide is well known.[13]

A mixture of 10 g. of the lactone, 20 g. of zinc dust and 100 cc. of glacial acetic acid was boiled for two hours, poured into water, and the precipitated solid filtered and recrystallized from acetone. It was identified as the low melting form (187°) of the acid VI by a mixed melting point, and conversion into the corresponding ester (155°). The same acid resulted if methanol was used as a solvent.

The lactone was unchanged after twenty-four hours of standing at room temperature in methanol, or after a week in chloroform or acetic acid, each saturated with hydrogen bromide, as well as after refluxing for two hours in acetic acid solution through which hydrogen bromide was passed. However, when 1 g. in 25 cc. of acetic acid, saturated with hydrogen bromide at room temperature, was heated in a sealed tube at 100° for eight hours it gave as the single product the high melting form (261°) of the acid VI, identified by mixed melting point and conversion into the ester (178°).

3. **Action of Ammonia: α,β-Diphenyl-γ-hydroxy-γ-benzoylbutyramide II.**—A suspension of 10 g. of the lactone in 125 cc. of absolute ethanol was saturated with dry ammonia; most of the solid dissolved. The supernatant liquid was decanted and left in a closed flask overnight; fine needles separated in a nearly quantitative amount. The amide melts with decomposition at about 202°, and after a few minutes at 205° all the ammonia has been evolved and the lactone re-formed. Recrystallization from glacial acetic acid, or heating with phosphorus pentoxide in xylene, also removes the ammonia.

Anal. Calcd. for $C_{23}H_{21}O_3N$: C, 76.8; H, 5.8; N, 3.9. Found: C, 76.0, 76.1; H, 5.5, 5.5; N, 3.7.

The cyclopropane III resulted when an absolute alcoholic solution of the amide, saturated with hydrogen chloride, was allowed to stand for a day. On recrystallization from a methanol–chloroform mixture it formed rods, m. p. 179°; a mixed melting point with an authentic specimen[2] was not depressed, and on dehydration it gave the cyclic nitrile, m. p. 166°. When dissolved in acetic anhydride containing a trace of sulfuric acid, and poured upon ice and sodium carbonate, the cyclic amide gave an oil, which, on long standing, became solid and proved to be the hydroxyamide.[14]

4. **Action of Magnesium Methylate; Methyl α,β-Diphenyl-γ-hydroxy-γ-benzoylbutyrate V.**—The magnesium methylate from 5 g. of magnesium and 80 cc. of methanol, and 25 g. of the lactone were shaken mechanically for an hour at room temperature and decomposed by pouring upon 400 g. of ice and 25 cc. of concd. hydrochloric acid. The pale yellow, oily solid was separated by the usual manipulations into a yellow oil and 6 g. of the 178° keto ester. After standing for several days, 1 g. of the hydroxy ester (180°) had separated and after several more days, 8 g. of the 118° isomer was collected. When the time of contact with the magnesium methylate was short, the quantity of the latter ester was higher, but if prolonged, more of the high melting isomer was found. The low melting form was isomerized to the other by fifteen minutes of shaking with cold magnesium methylate but the 180° variety was unchanged by this reagent. From the residual oils were isolated high melting ketoacid, unchanged lactone, and benzaldehyde. Sodium methylate brought about removal of alcohol and reformation of the lactone.

The esters were recrystallized from methanol, from which they separated as fine rods, melting at 180 and 118°.

Anal. Calcd. for $C_{24}H_{22}O_4$: C, 77.0; H, 7.9; OCH_3, 8.3. Found: (180°) C, 76.8, 76.8; H, 7.8, 7.8; OCH_3, 8.6; (118°) C, 76.6, 76.5; H, 7.6, 7.7; OCH_3, 8.4, 8.5.

Reactions.—(a) The esters were heated in an apparatus arranged to sweep out and condense any gas formed. At 190°, each ester evolved methanol (identified as the 3,5-dinitrobenzoate) and left the lactone as a residue. (b) On treatment of the high melting form in boiling methanol

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[13] Kröhnke and Timmler, *Ber.*, **69**, 614 (1936).

[14] The "stereoisomeric amide"[2] (p. 161) is really this hydroxyamide; thus there is a little ring opening of the cyclopropane by sulfuric acid.

with 2,4-dinitrophenylhydrazine and a little hydrochloric acid, and allowing to stand, bright red rods of a dinitrophenylhydrazone (B) separated and were filtered; the filtrate then deposited yellow leaflets, the dinitrophenylhydrazine (A) of the lactone. Under the same conditions, the 118° ester gave only derivative A. When a chloroform solution of B containing a little hydrogen chloride was refluxed, the substance was converted into A, whereas in methanol A was partially converted into B. The derivative B crystallized from methanol in red rods, m. p. 224°.

Anal. Calcd. for $C_{30}H_{26}O_7N_4$: N, 10.1. Found: N, 10.0, 9.9.

(c) The acetate of the 180° ester was obtained by allowing an acetyl chloride solution of the ester to evaporate spontaneously after standing for sixteen hours, but it was necessary to reflux the 118° form for four hours to get the derivative. Both were recrystallized from methanol. The acetate of the 180° ester formed rods, m. p. 145°, while its isomer separated in rosets of rods, m. p. 132°.

Anal. Calcd. for $C_{26}H_{24}O_5$: C, 75.0; H, 5.8; OCH_3, 7.4. Found: C, 74.8, 74.7; H, 5.8, 5.9; OCH_3, 7.5.

5. Action of Sodium Methylate. (a) 2,4,5-Triphenyl-1,3-diketocyclopentene-4, VII.—A suspension of 20 g. of the lactone in 300 cc. of methanol, containing the methylate from 4 g. of sodium, was shaken for ten hours when all had dissolved. The dark brown solution was decomposed by adding to dilute acetic acid and the semi-solid mass that separated was filtered. After trituration with methanol the bright yellow solid that remained undissolved was filtered, and recrystallized from a 2:1 methanol–chloroform mixture. It formed fine, yellow rods, m. p. 166°; the yield was 6.5 g. or 32%. It was not found when sodium or potassium hydroxide was used instead of sodium methylate. A Zeisel determination was negative.

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.2; H, 4.9. Found: C, 85.3, 85.4; H, 5.1, 5.3.

(b) Other Products.—After several months of standing, the only other solid that had separated was unchanged lactone, so a chloroform solution of the oil was submitted to a systematic extraction with sodium bicarbonate, potassium carbonate, copper acetate and sodium hydroxide, and then given a water wash. Nothing was obtained from the potassium carbonate or copper acetate, but the substances listed were found as indicated: (1) from the bicarbonate, the high melting acid VI and diphenylmaleic anhydride; (2) from the sodium hydroxide, high melting form of diphenylsuccinic acid; (3) from the final water wash, the lactone VIII; (4) by steam distillation of the residual oil, benzaldehyde. The oil gave no phenylhydrazone or phenacyl ester. It decomposed badly on attempted vacuum distillation; from the distillate were isolated benzoic acid, acetophenone and stilbene, obviously decomposition products. An unexplained phenomenon was the production of a green color in the chloroform during the sodium hydroxide wash, while the latter became orange. When the green solution was washed with water, the latter became green and the chloroform turned yellow. On greatly diluting the wash water, the unsaturated lactone VIII separated. On acidifying this basic solution, a thick yellow oil was obtained, but beyond noting its lactonic nature (insoluble in carbonates, soluble in hydroxides) nothing definite was learned.

The identification of each substance was assured by comparison with authentic specimens at hand or prepared by directions in the literature; *e. g.*, diphenylmaleic anhydride, m. p. 154°,[15] the unsaturated lactone VIII, m. p. 175°,[6] and diphenylsuccinic acid, m. p. 229°.[15b]

B. Reactions of the Unsaturated Lactone VIII.—For further identification, and for purposes of obtaining reference samples, the action of ammonia to form a hydroxy amide XIII, m. p. 199–201° dec., and a lactam XIV, m. p. 241°, reduction by hydrogen iodide to give α,β-diphenyl-γ-benzylcrotolactone XVI, m. p. 127–128°,[6] and alkaline fusion to give the lactol XII, m. p. 181°, were repeated and confirmed. The drastic procedure in the latter reaction is unnecessary; one only needs to acidify the solution of the sodium salt at room temperature with dilute acetic acid and recrystallize from this reagent, to obtain the lactol at will. To dehydrate, it may be recrystallized from anhydrous solvents—the phosphorus oxychloride treatment is unnecessary.

The new reactions determined were reduction by zinc and acetic acid (one hour) which gave the dihydro derivative XVI, hydration and dehydration, just described, and the action of alkaline solutions.

(1) A solution of 2 g. of the lactone in 30 cc. of absolute alcohol containing 0.4 g. of potassium hydroxide was refluxed for twenty-four hours and the mixture distilled with steam. The distillate contained benzaldehyde, which was identified as the phenylhydrazone (0.05 g., m. p. 156°). After acidification to remove the reagent, the distillate was shaken with ether, to remove toluene, if present, but nothing was found in the extract. From the residual solution in the steam distillation flask, 0.8 g. of unchanged lactone was recovered, and, on adding acetic acid, 0.6 g. of diphenylmaleic anhydride was obtained.

(2) A similar solution containing an equivalent of sodium ethylate turned purple on an hour's boiling and the diketone VII was isolated after acidification. On shaking 1 g. of the lactone with 15 cc. of absolute methanol containing 9.2 g. of sodium for ten hours, the solution became purple, but 0.65 g. of lactone was still undissolved. From the colored solution, 0.25 g. of the diketone was isolated on acidification.

C. Reactions of the Diketone VII.—In the Grignard machine, the diketone evolved one equivalent of methane and slowly consumed three moles of reagent.

(1) The 2,4-dinitrophenylhydrazone was prepared in the usual manner; it separated from a methanol–chloroform mixture in fine, orange needles, m. p. 235°.

Anal. Calcd. for $C_{29}H_{20}O_5N_4$: N, 11.1. Found: N, 11.1, 11.1.

(2) Alkaline Reagents.—The diketone dissolves in alcoholic sodium or potassium hydroxide and in alcoholates, producing a deep purple color, and is recovered on acidification. After prolonged refluxing (twenty-four hours) as in (1) above, it gave the same products.

(3) Alcoholic Ammonia.—A mixture of 1 g. of the diketone and 15 cc. of alcohol was saturated with ammonia at 0° and heated at 100° in a sealed tube for six hours. The initially formed deep purple color changed to brown. On

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(15) Reimer, (a) *Ber.*, **13**, 742 (1880); (b) *ibid.*, **14**, 1802 (1881).

opening, crystals of the lactam XIV were filtered, and on concentrating the solution and decoloring by Nuchar, a mixture of the hydroxy amide XIII and lactam separated; they were identical with the specimens prepared above. Meyer[16] has made an extensive study of the action of ammonia on a variety of lactones and in no case was an amino acid obtained, but only hydroxy amides or lactams.

(4) Reduction; α,β-Diphenyl-γ-benzalbutyric Acid XV.—(a) A mixture of 10 g. of the diketone, 200 cc. of acetic acid and 20 g. of zinc dust was refluxed for a half hour; the yellow color had disappeared after ten minutes. It was filtered into 400 cc. of water and the precipitated acid collected; 9 g. was obtained after one recrystallization from methanol. It forms white needles, m. p. 204–205°.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.1; H, 6.0; mol. wt., 328. Found: C, 83.9; H, 5.8; mol. wt., 345.

(b) A mixture of 2 g. of the diketone, 1 g. of red phosphorus and 10 cc. of constant boiling hydriodic acid was refluxed for two hours and decanted from the resinous deposit. The latter was treated by sodium bisulfite several times and then the organic material extracted with hot methanol and worked up as above; the same acid resulted. It was soluble in aqueous carbonate and recovered unchanged on acidification. An acetone solution instantly decolorized permanganate, and a chloroform solution instantly added bromine. It did not give a carbonyl derivative.

(c) The chromic acid oxidation was performed in acetic acid in the usual manner; the isolation of diphenylsuccinic acid was difficult, owing to the unfavorable nature of the material. It was eventually purified and shown to be the high melting isomeric form of diphenylsuccinic acid by melting and mixed melting point (229°). A permanganate oxidation was carried out in such a way that the benzaldehyde could be distilled as formed; identification was made through the phenylhydrazone. From the residual solution the same diphenylsuccinic acid was isolated.

(5) Oxidation. (a) The Bimolecular Product.—To a solution of 0.4 g. of selenium dioxide in 15 cc. of boiling dioxane was added 1 g. of the diketone and the whole refluxed with stirring for one and one-half hours. After filtering, the solution was poured into water, ammonium chloride added to hasten coagulation and the solid filtered. It was recrystallized from chloroform–methanol, and formed microscopic yellow prisms, m. p. 247°; the yield was nearly quantitative.

Anal. Calcd. for $C_{46}H_{30}O_4$: C, 85.6; H, 5.3; mol. wt., 646. Found: C, 85.0; H, 5.1; mol. wt., 716.

The same substance was obtained, along with benzoic acid, by the action of chromic acid, with benzaldehyde and unreacted lactone from dilute sulfuric acid at water-bath temperature, and from the mixture resulting on ozonization in ethyl bromide. Permanganate, however, destroyed the molecule completely, giving benzaldehyde, benzoic acid and carbon dioxide. Dilute nitric acid gave oils and a little *p*-nitrobenzoic acid. Potassium hypobromite was without action.

(b) Hydrogen Peroxide Product.—To a solution of 0.5 g. of the diketone in 15 cc. of acetone, 10 cc. of 30% hydrogen peroxide was added; this precipitated the diketone. A 10% solution of potassium hydroxide was then added, dropwise from a buret, each drop being admitted only after the deep purple coloration was discharged by shaking; this took 0.3 cc. and a period of an hour. A yellow precipitate (0.3 g.) was filtered and recrystallized from methanol; it formed yellow prisms, m. p. 185°.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.2; H, 4.7; mol. wt., 340. Found: C, 81.0, 81.2; H, 4.5, 4.5; mol. wt., 372.

The new substance is soluble in warm, aqueous sodium hydroxide, does not decolorize bromine and is unaffected by hydrogen chloride in acetic acid. It did not give a dinitrophenylhydrazone.

A solution in acetyl chloride gave a new yellow solid on evaporation, which separated from methanol–chloroform in rods, m. p. 155°.

Anal. Found: C, 80.0, 79.8; H, 4.9, 4.8.

A Zeisel determination was negative; it did not contain halogen. The composition shows fair agreement with $C_{50}H_{34}O_7$, a diacetate of a dehydrated bimolecular product.

D. Synthesis.—To a warm solution of 6.1 g. of dibenzyl ketone and 5 g. of ethyl benzoylformate in 15 cc. of absolute alcohol was added the freshly prepared sodium ethylate from 0.6 g. of sodium and 15 cc. of alcohol (absence of water is essential) and the solution refluxed. It at once became deep yellow and after fifteen minutes a solid began to separate.[17] After an hour it was acidified with acetic acid and the pale yellow lactone filtered; the average yield of several runs was 3 g. or 27%. It was best recrystallized from *n*-propanol. By acidifying with diluted acid, the lactol could be isolated. When the same amounts of reactants were taken but in methanol, using enough of the latter to keep everything in solution, a deep purple color was noted and after two hours of acidification gave the diketone in a 40% yield. With larger quantities an excess of sodium methylate is advisable.

With the same amounts but 0.5 g. of piperidine or a trace of sodium ethylate as a catalyst, white needles of the ester XVII shortly separated. The first crop weighed 3.5 g., and on standing and evaporation, successive amounts were obtained. It recrystallized from ethanol in fine needles, m. p. 128°.

Anal. Calcd. for $C_{25}H_{24}O_4$: C, 77.3; H, 6.2; OC_2H_5, 11.6. Found: C, 77.0, 69.9; H, 6.0, 5.1; OC_2H_5, 11.4, 11.7.

This ester gave only oils with alcoholates.

After refluxing for four hours with acetyl chloride, an acetate resulted; this was very soluble in the usual solvents. It separated from methanol in rods of m. p. 101°.

Anal. Calcd. for $C_{27}H_{26}O_5$: C, 75.3; H, 6.0. Found: C, 75.1, 75.1; H, 6.0, 6.1.

(6) Other Reagents.—The lactone was unaffected by ozone and only slightly attacked by chromic acid. Bromine was decolorized very slowly, with some evolution of hydrogen bromide; 40% of the lactone was recovered, while the remainder of the reaction product was a sticky gum.

This work has been assisted by a generous grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

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[16] Meyer, *Monatsh.*, **20**, 717 (1899).

[17] The white sodium salt sometimes separated if the amount of solvent was less.

Summary

1. When dissolved in alkaline solutions, α,β-diphenyl-γ-butyrolactone undergoes a diversified series of reactions, involving oxidation and reduction, cleavage and hydrolysis.

2. Among new products are a pair of stereoisomeric ketohydroxyesters and a highly phenylated cyclopentadienone.

3. The latter is capable of a great variety of reactions; in general, it shows a marked resemblance to 2-phenylindandione-1,3.

MONTREAL, CANADA RECEIVED JANUARY 11, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

Gamma-Benzoylbutyronitrile

BY C. F. H. ALLEN AND W. L. BALL

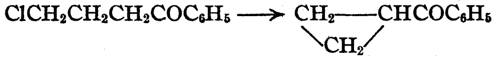
Up to the present time all δ-ketonic nitriles (I) investigated have been highly substituted[1]

$$\begin{matrix} RCHCH_2COR \\ | \\ RCHCN \end{matrix} \qquad \begin{matrix} CH_2CH_2COC_6H_5 \\ | \\ CH_2CN \end{matrix}$$

I II

Therefore it was of interest to prepare the simplest member of the series, γ-benzoylbutyronitrile (II), and compare its properties with those of the more complex homologs.

There are several series of reactions that might be expected to yield the desired nitrile, but those that seemed to involve the fewest steps and utilize readily available materials gave other products. Thus, the action of potassium or cuprous cyanide on γ-chlorobutyrophenone was to remove hydrogen chloride, giving an excellent yield of benzoylcyclopropane.[2]



$$ClCH_2CH_2CH_2COC_6H_5 \longrightarrow \underbrace{CH_2\text{——}CHCOC_6H_5}_{\diagdown CH_2 \diagup}$$

The nitrile was finally obtained by dehydration of the corresponding amide (III) in a particular manner; the amide was secured from γ-benzoylbutyric acid by the following series of reactions

$$C_6H_5COCH_2CH_2CH_2COOH \longrightarrow$$
$$C_6H_5COCH_2CH_2CH_2COOCH_3 \xrightarrow{NH_3}$$
$$C_6H_5COCH_2CH_2CH_2CONH_2{\cdot}NH_3 \longrightarrow$$
$$C_6H_5COCH_2CH_2CH_2CONH_2$$

Kugel[3] prepared the lower homolog, β-benzoylpropionamide, in a similar manner, though Biedermann[4] had obtained cyclic compounds by a like procedure. Our results resembled those of Kugel and will be described in the experimental part.

The nitrile forms carbonyl derivatives and is very easily hydrolyzed to γ-benzoylbutyric acid; it is possible to arrest the hydrolysis at the intermediate amide stage. It reacts with bromine with immediate evolution of hydrogen bromide; most of the reaction product is an untractable oil, but a small amount of 2-phenyl-α-pyridone (VI) can be isolated.

The two characteristic properties of δ-ketonic nitriles are isomerization to a tetrahydropyridine (through the amide) on treatment with mineral acids in indifferent media, and the formation of 2-bromopyridines on bromination in acetic acid.[1a] As mentioned above, it was not possible to determine completely the course of bromination of γ-benzoylbutyronitrile. The formation of the 2-phenylpyridone is probably best explained as follows: the nitrile is isomerized to the cyclic isomer by some of the hydrogen bromide evolved, the hydropyridine then being dehydrogenated to the pyridone by bromine in the usual manner.[1a] This mechanism could not be confirmed, since no pyridone resulted when the pure cyclic substance was brominated in a similar manner.

All attempts at isomerization gave either the amide or the acid; this is not a real difference because it has been shown that the hydropyridine formation proceeds through the amide.[1b] The reactions are thus essentially the same as with the substituted homologs, but owing to less favorable physical properties, all the products cannot be determined.

The isomeric tetrahydropyridine (V) can be obtained in a variety of ways; in fact, it is usually obtained by reactions that might be expected to yield the nitrile, *e. g.*, dehydration of the amide

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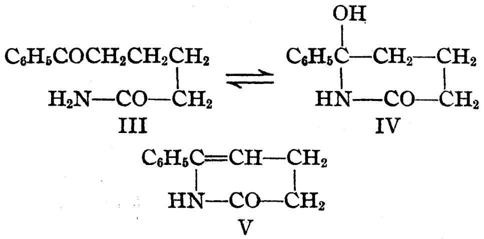
[1] (a) Kohler, Graustein and Merrill, THIS JOURNAL, **44**, 2536 (1922); Kohler and Souther, *ibid.*, p. 2903; Kohler and Allen, *ibid.*, **46**, 1522 (1924); (b) Allen, *ibid.*, **47**, 1733 (1925); **49**, 1112 (1927); Allen and Bell, *Can. J. Research*, **11**, 40 (1934); Allen and Scarrow, *ibid.*, p. 395. (c) Corson, Dissertation, Harvard University, 1924; Lowry, *ibid.*, 1924.

[2] Allen and Boyer, *Can. J. Research*, **9**, 159 (1933).

[3] Kugel, *Ann.*, **299**, 50 (1897).

[4] Biedermann, *Ber.*, **24**, 4074 (1891).

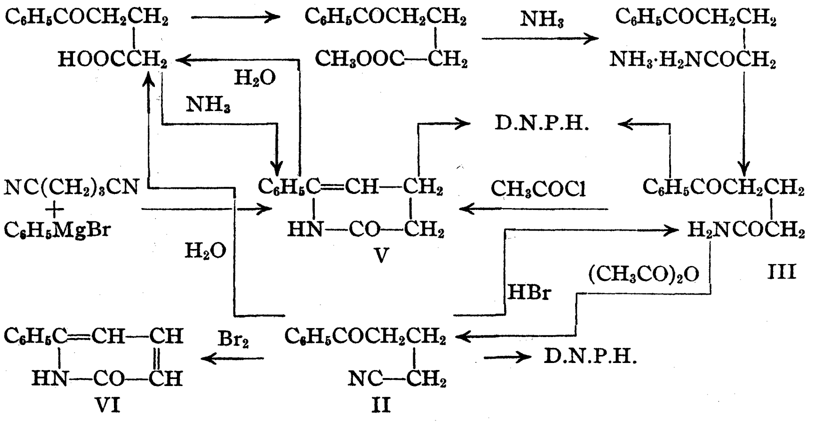
by the use of acetyl chloride or by heating alone, or from the reaction between phenylmagnesium bromide and glutaronitrile. The relative ease of formation may indicate that the amide exists as one component of a tautomeric mixture (III $\rightleftharpoons$ IV)



In the case of other delta ketonic amides, the available evidence points to their existence only in the cyclic form.[1b,5]

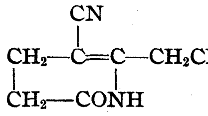
The reactions of the cyclic form (V) are in accordance with the structure written. Thus, acid hydrolysis leads to γ-benzoylbutyric acid. It decolorizes bromine instantly; after about two-thirds of the calculated amount of bromine has been added, hydrogen bromide begins to be evolved. A bromide–bromate titration shows one double bond. When treated with 2,4-dinitrophenylhydrazine in the usual manner (acid solution) the ring is opened with addition of a molecule of water, and the dinitrophenylhydrazone of the amide is obtained.

These reactions are conveniently summarized in the flow-sheet.



D.N.P.H. = 2,4-Dinitrophenylhydrazone.

Bruylants[6] has examined the action of several Grignard reagents on glutaronitrile and, among the numerous products, found substances which he believed to be open chain δ-ketonic nitriles; thus, he wrote structure (II) for the substance obtained when phenylmagnesium bromide was used. We have repeated the reaction following Bruylants' directions and isolated the product having the properties[7] as described, and found it to be identical with (V), the cyclic isomer of (II). It is easy to understand the confusion, for both give the same hydrolysis product and react with bromine, the tests employed by Bruylants; the differences on bromination would hardly be noticed unless one were expecting them. Aliphatic Grignard reagents brought about condensation, and gave, as the principal product, a substance $C_{10}H_{11}ON_3$, for which he wrote an open chain keto-trinitrile structure; from the available data, supplemented by the results just mentioned, it probably should have the ring formula (VII).



VII

Experimental

A. Action of Ammonia on Methyl γ-Benzoylbutyrate; γ-Benzoylbutyramide, III.—Cyclopentanone was oxidized to glutaric acid by 50% nitric acid;[8] the latter was dehydrated by acetic anhydride[9] and converted into γ-benzoylbutyric acid by the Friedel–Crafts reaction.[10] A mixture of 5 g. of the methyl ester,[11] 10 cc. of alcohol and 50 cc. of concd. ammonium hydroxide were shaken mechanically for four hours, and the solvent allowed to evaporate; a solid of m. p. 110–125° separated. A similar product resulted after spontaneous evaporation of a solution of 25 g. of the ester in 75 cc. of alcohol that had been saturated with ammonia. This solid was dissolved in a slight excess of a warm 1:1 mixture of chloroform and ether; on cooling, white needles, m. p. 118–120°, separated from a purple solution. Two recrystallizations from benzene raised the melting point to 120–121°. By continued reworking of all filtrates, additional amounts of solid of varying degrees of homogeneity resulted.

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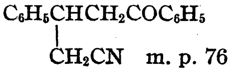
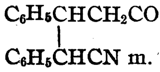
[5] Barat, *J. Ind. Chem. Soc.*, **7**, 321 (1930).

[6] Bruylants, (a) *Bull. soc. chim. Belg.*, **32**, 307 (1923); (b) *Bull. sci. acad. roy. Belg.*, [5] **7**, 252 (1921); (c) Bruylants and Dewail, *ibid.*, [5] **12**, 464 (1926).

[7] Bruylants gave the melting point as 158°. This seemed to us surprisingly high for an unsubstituted nitrile, when compared with the melting points of the phenylated homologs,[1a,c] but in accord with a cyclic structure. We



$\underset{\displaystyle CH_2CN}{C_6H_5CH}CH_2COC_6H_5$ m. p. 76°



$\underset{\displaystyle C_6H_5CHCN}{C_6H_5CH}CH_2COC_6H_5$ m. p. 103, 118°

have found that the melting point of γ-benzoylbutyronitrile is 38°.

[8] *Organic Syntheses*, **14**, 90 (1934).

[9] Sircar, *J. Chem. Soc.*, 898 (1928).

[10] *Organic Syntheses*, **13**, 12 (1933).

[11] Allen and Cressman, THIS JOURNAL, **55**, 2953 (1933).

This substance was unstable; after standing overnight the melting point became much less sharp. It evolved ammonia on being heated; it decolorized bromine and permanganate on warming with the reagents in appropriate solvents. It dissolved in warm chloroform, carbon tetrachloride, and benzene to give a reddish solution; if not cooled at once, a colorless solid, m. p. 140–142°, separated; treatment with boiling water gave this same substance. This was the amide III, which, when pure, formed flat rods, m. p. 144°. The amide was also obtained from the purple melt of the 120° solid, and from the various oily by-products by repeating the ammonia treatment, dissolving the dark oil in benzene and decolorizing with charcoal. The total yield was thus raised to 70%.

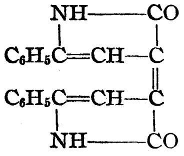
Anal. Calcd. for the ammonia addition product: (a), $C_{11}H_{16}O_2N_2$: C, 63.5; H, 7.7; N, 13.5; for the amide III, $C_{11}H_{13}O_2N$: C, 69.1; H, 6.8; N, 7.3. Found: (A), C, 63.9; H, 7.6; N, 13.8; (III) C, 69.4; H, 6.8; N, 7.3.

The amide was hydrolyzed easily to γ-benzoylbutyric acid. The 2,4-nitrophenylhydrazone of the amide was prepared in the usual manner; it separated from a methanol–ethyl acetate mixture in clusters of orange rods having square ends, m. p. 195–196°.

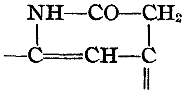
Anal. Calcd. for $C_{17}H_{17}O_5N_5$: N, 18.8. Found: N, 18.6.

A mixed melting point with the reagent (m. p. 198°) was depressed 20°.

With a view to securing a higher yield in the alcohol–ammonia method, the saturated solution was allowed to stand for three weeks; it became a deep red, then purple. A small amount of a black, crystalline solid was removed; from the solution a poor yield of amide and ammonia addition product were separated. The black solid did not melt below 320°, but sublimed in brown fumes when heated on porcelain. It gave a blue solution in concd. sulfuric acid, being precipitated unchanged on dilution, but dissolved to a colorless solution in sodium hydroxide. In all its properties it resembles Kugel's product obtained from ammonia and ethyl β-benzoylpropionate[3] for which he wrote the structure VIII.



VIII



IX

By analogy, our substance would be the homolog IX; it was not investigated further.

B. γ-Benzoylbutyronitrile, II.—A solution of 5 g. of the amide in 25 cc. of acetic anhydride was unchanged after being allowed to stand overnight, but on refluxing an hour and distilling *in vacuo*, an oil, b. p. 135–140°, at 10 mm., was obtained; this solidified on standing, only if a pure amide had been used. The yield was 3.5 to 4.9 g. (82–94%); it is very soluble in the usual solvents. It formed plates, m. p. 38°.

Anal. Calcd. for $C_{11}H_{11}ON$: C, 76.3; H, 6.4. Found: C, 76.2, 76.0; H, 6.4, 6.5.

The 2,4-dinitrophenylhydrazone separated as red-brown plates from (1:2) alcohol–ethyl acetate, m. p. 173–175°.

Anal. Calcd. for $C_{17}H_{15}O_4N_5$: N, 19.9. Found: N, 19.5.

The semicarbazone, prepared in the usual way, separated from chloroform as plates, m. p. 176–177°. It is only sparingly soluble in alcohol.

Anal. Calcd. for $C_{12}H_{14}ON_4$: N, 24.3. Found: N, 24.1.

The nitrile was easily hydrolyzed to γ-benzoylbutyric acid in moist solvents in the presence of acid. When a solution in chloroform (that had been dried with calcium chloride) was saturated with hydrogen bromide and allowed to stand overnight, a brownish paste remained as the green solution evaporated. When this was washed with dry ether, a white solid (m. p. 205–210°—a red liquid) that could not be purified, remained; treatment with alcohol or acetic acid gave γ-benzoylbutyric acid. If the white residue was dissolved in absolute alcohol containing freshly fused potassium acetate, and evaporated to dryness, the benzene extract deposited the amide III. The properties of the white substance agree with those of an "imide bromide."

Bromination is described in section D.

C. 2-Keto-6-phenyl-1,2,3,4-tetrahydropyridine, V.—This substance was obtained in several ways. The purest product resulted on refluxing an acetyl chloride solution of the amide for a half hour, filtering the solid, and washing it with dry ether. On vacuum distillation, the oily residue gave a further quantity. The properties agreed with those given by Bruylants[6] but repeated recrystallization of crude material was necessary to get a pure substance; dry benzene or carbon tetrachloride was found preferable to alcohol.

The cyclic compound was also obtained in the following ways, the identification in each case being by mixed melting point and comparable behavior in solvents: (a) when the amide was heated alone, the melt changed colors, blue, red, brown; the residue was taken up in alcohol and decolorized by charcoal; (b) dry ammonia was passed through molten γ-benzoylbutyric acid at 160–170° for nine hours;[12] (c) by repetition of Bruylants' directions, through the action of phenylmagnesium bromide on glutaronitrile.

The tetrahydropyridine was shown to have one double bond by titration; 0.200 g. used 0.195 g. of bromine (calcd., 0.185 g.). Hydrolysis gave γ-benzoylbutyric acid. The action of nitrous acid was indeterminate. On treatment with 2,4-dinitrophenylhydrazone in the usual manner (acid solution) the derivative of the amide III resulted. Bromine gave oils.

D. 2-Phenyl-α-pyridone, VI.—An excess (3 g.) of bromine was added to 3 g. of γ-benzoylbutyronitrile in 50 cc. of chloroform; the solution turned black and hydrogen bromide was evolved. The solvent was removed on the steam-bath and the residue distilled *in vacuo*, since preliminary attempts had shown the futility of any other kind of manipulation. At 20 mm. a preliminary, nondescript fraction came over up to 180°, but from the second (mostly at 190°) a solid separated; the latter was very soluble in benzene, carbon tetrachloride, and chloroform, soluble in hot water but insoluble in cold, and recrystal-

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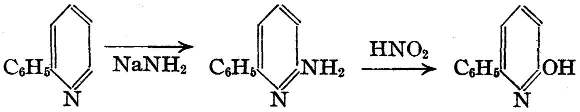
[12] Work of Mr. L. F. Somerville.

lized best from methanol in flat rods with square ends, m. p. 195°; although it appeared to crystallize well from petroleum ether the melting point was lower by 10°. A hydrochloride of m. p. 101–103° was prepared as directed in the literature, which gave the melting point 104°. All the properties agree with those described by Leben.[13] In order to establish the identity with certainty, a specimen was prepared as directed in the literature,[14,15] the melting point was not depressed on admixture.

Owing to the roundabout method of synthesis, several attempts were made to obtain it by a simpler procedure, but without success. It was relatively easy to prepare 2-aminopyridine and 2-phenylpyridine but impossible to introduce both groups into the same molecule. The action of sodium amide on 2-phenylpyridine led to a high melting, bimolecular product.



This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

γ-Benzoylbutyronitrile has been prepared by the dehydration of the corresponding amide with acetic anhydride. Other dehydrating agents gave a cyclic, isomeric derivative of tetrahydropyridine. The characteristic properties of each have been determined.

MONTREAL, CANADA RECEIVED FEBRUARY 8, 1937

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(13) Leben, *Ber.*, **29**, 1673 (1896).

(14) Kalff, *Rec. trav. chim.*, **46**, 594 (1927).

(15) In this work we were assisted by Mr. J. C. W. Evans. Some of the preliminary steps were first carried out by Dr. A. C. Bell. Their aid is gratefully acknowledged.

[CONTRIBUTION FROM THE ORGANIC RESEARCH LABORATORY, CHEMISTRY DEPARTMENT, UNIVERSITY OF THE PHILIPPINES]

On the Naturally Occurring Linolic Acid in Cottonseed and Soya Bean Oils and the Regenerated Linolic Acid from Alpha Linolic Acid Tetrabromide of These Oils

BY D. M. BIROSEL

In a previous paper,[1] it was reported that only two isomeric linolic acid tetrabromides were isolated from the products of direct bromination of the free fatty acids of lumbang or candle nut (*Aleurites moluccana*) oil and of the regenerated linolic acid; that only two tetrahydroxystearic acids were isolated from the products of oxidation with alkaline permanganate solution of the free fatty acids of lumbang oil and of the regenerated linolic acid; and that the β- and δ-linolic acid tetrabromides which have been reported by other workers as obtainable from the bromination product of the free fatty acids of lumbang oil are ethyl ester mixed with varying amount of free solid acid tetrabromide.

Considerable work[2] has been done on linolic acid but the literature presents conflicting observations and conclusions. The present work is primarily intended to supplement the observations previously recorded by the writer. It is desired to report in this paper the observations made on linolic acid naturally present in soya bean and in cottonseed oils and on the regenerated linolic acid from α-linolic acid tetrabromide prepared by direct bromination of the free fatty acids of these oils.

From the direct bromination of the dried free fatty acids of soya bean and cottonseed oils, using ether as reaction medium and low boiling point petroleum ether[3] as vehicle of crystallization, α-linolic acid tetrabromide (m. p. 114°) was the only

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(1) Birosel, *Natural and Applied Science Bulletin of the University of the Philippines*, **2**, 103 (1932).

(2) Meyer and Beer [*Monatsh.*, **33**, 325 (1912)] obtained β-sativic acid of m. p. 174° and α-sativic acid of m. p. 163° from the oxidation with cold alkaline permanganate solution of the free fatty acids of "Jimson weed" *Datura Stramonium*. Nicolet and Cox [THIS JOURNAL, **44**, 144 (1922)] doubted the existence of these sativic acids on the ground that the fatty acids of Jimson weed seeds yield α-linolic acid tetrabromide, m. p. 117°, whereas the highest melting point recorded in the literature is 114°. A. P. West and co-workers [*Philippine J. Sci.*, **32**, 41 (1927); *cf. C. A.*, **21**, 1720 (1927); *ibid.*, **32**, 297 (1927); *cf. C. A.*, **21**, 2250 (1927); *ibid.*, **42**, 251 (1930)] reported having isolated three solid linolic acid tetrabromides from the free fatty acids of lumbang oil. They claimed that their β-linolic acid tetrabromide corresponds to the compound which was reported by Takahashi [*J. Tokyo Chem. Sci.*, **4**, 233 (1919); *C. A.*, **13**, 1583 (1919)] but regarded their α-linolic acid tetrabromide of lumbang oil as different from a similar compound from soya bean oil on the ground that their regenerated linolic acid did not yield the β-linolic acid tetrabromide of Takahashi. Birosel[1] has shown that the β- and δ-linolic acid tetrabromides of West are ethyl ester of the acid mixed with varying amount of free α-linolic acid tetrabromide.

(3) Birosel[1] reported that with ethyl alcohol as vehicle of crystallization for the crude solid acid tetrabromide, the β- and δ-acids of West[2] were obtained whereas if low boiling petroleum ether was used none was obtained. West's[2] compounds were also obtained when pure α-linolic acid tetrabromide, m. p. 114°, was refluxed with ethyl alcohol until oil separated upon cooling the solution. The supposedly β- and δ-acids did not give neutralization value but their alcoholic solutions to which a few drops of phenolphthalein solution were added turned red upon addition of the first drop of standard alkali.

solid tetrabromide[4] isolated from the bromination products.

When the linolic acid regenerated from the α-linolic acid tetrabromide prepared from the free fatty acid of soya bean oil by direct bromination, was subjected to the action of bromine in the proper way, and using petroleum ether as crystallization medium, α-linolic acid tetrabromide,[5] m. p. 114°, was the only solid product obtained. No solid acid tetrabromide of lower melting point was isolated.

On oxidizing the free fatty acid of soya bean and cottonseed oils with cold alkaline permanganate solution, only two tetrahydroxystearic acids[6] were isolated. The corresponding acids prepared from the two oils have identical melting points.

Oxidation with cold alkaline permanganate solution of the regenerated linolic acid from the α-linolic acid tetrabromide (m. p. 114°) prepared from the free fatty acids of cottonseed and soya bean oils by direct bromination gave α-sativic acid (m. p. 164°) and β-sativic acid (m. p. 174°).

It is thus seen that the observations previously made by the writer on the naturally occurring linolic acid in lumbang oil and on the regenerated linolic acid from α-linolic acid tetrabromide prepared from the said oil by direct bromination find support in the experimental observations recorded in this paper.

Experimental Part

Soya Bean Oil.—This oil was prepared from soya bean seed by extraction with ether in the usual way. A liter of oil was prepared.

Preparation of Free Fatty Acids of Soya Bean Oil.—Five hundred grams of soya bean oil was treated in the usual way with a little more than the equivalent amounts of potassium hydroxide in aldehyde-free alcohol solution. When a homogeneous product after digestion on the steam-bath was obtained, the alcohol was distilled off and the soap solution was treated with excess dilute sulfuric acid. The mixture was digested to complete hydrolysis. The oil which floated was separated and taken with ether and washed several times with water until the washing was neutral. The ethereal solution was dried with anhydrous sodium sulfate, after which it was filtered and the solvent distilled. The residue which was free from solvent was further dried in a desiccator.

Preparation of α-Linolic Acid Tetrabromide.—Two hundred and twenty-eight grams of the dried free fatty acid of soya bean oil was dissolved in two liters of dry ether in a three-necked, round-bottomed flask of three-liter capacity. The solution was cooled down to −10°, with ice–salt mixture. Sixty-five cc. of bromine was added slowly while the solution was stirred mechanically. The temperature was not allowed to rise above 0°. Bromination took four hours to complete. Due to excess bromine, the solution was orange in color. The ether-insoluble precipitate was filtered off and washed with the same solvent. The filtrate and washing were washed together with dilute sodium thiosulfate solution until the color disappeared. The ethereal solution was dried with anhydrous sodium sulfate and filtered. The solvent was distilled off and the residue was taken up in low boiling petroleum ether from which the α-linolic acid tetrabromide separated on cooling. The compound was found to melt at 111–113°. Two recrystallizations in the same solvent increased the melting point to 114°.

After exhausting the mother liquor of its α-linolic acid tetrabromide content, it was worked out for other solid tetrabromides of lower melting points. None was isolated from the mother liquor and from the concentrated filtrate of recrystallization.

Preparation of Linolic Acid.—Twenty grams of the α-linolic acid tetrabromide (m. p. 114°) was refluxed with zinc in 8% alcoholic solution of hydrochloric acid for seventy-two hours continuously. The ester of the regenerated unsaturated acid was saponified with excess potassium hydroxide and the soap solution was hydrolyzed with dilute hydrochloric acid. The oil that separated out was taken up in ether and the ethereal solution was washed several times with distilled water and then dried with anhydrous sodium sulfate, after which it was filtered and washed with anhydrous ether. The filtrate and washing were distilled together, after which the residue was dried in the desiccator. In all these operations care was exercised to prevent loss of product. The dried residue weighed 9.662 g. From the figures the percentage yield and purity of the product is 98%. This percentage was checked by the result of a subsequent reduction.

Linolic Acid Tetrabromides from the Regenerated Linolic Acid.—9.55 grams of the regenerated linolic acid was brominated as described above. Care was exercised to avoid missing products previously reported by Takahashi.[5] Using petroleum ether as vehicle of crystallization, I obtained from the first crystallization a product which melted sharply at 114°. The amount of α-linolic acid tetrabromide was 8.8 g., which represents 45% of the regenerated linolic acid used. No solid tetrabromide of lower melting point was isolated from the mother liquor from which liquid γ-linolic acid was obtained.

Oxidation of the Free Fatty Acids of Soya Bean Oil.—Fifteen grams of the dried fatty acids of soya bean oil was oxidized with cold alkaline permanganate solution according to the procedure of Rollet.[7] The acid was treated with a little excess more than the equivalent amount of potassium hydroxide and the soap was dissolved in two liters of water. Twenty-two grams of potassium permanganate was dissolved and made up to one liter of solution. This

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(4) Reformatzky, *J. prakt. Chem.*, **41**, 529 (1890); Hazura, *Monatsh.*, **9**, 180 (1888), and others, obtained only one solid linolic acid tetrabromide on brominating linolic acid.

(5) Takahashi[2] obtained β-linolic acid tetrabromide, m. p. 60°, from the regenerated linolic acid of α-linolic acid tetrabromide of soya bean oil. When petroleum ether was used as vehicle of crystallization as was done in this work no β-acid tetrabromide was isolated.

(6) Meyer and Beer[2] and Birosel[1] have obtained only α-sativic acid, m. p. 163°, and β-sativic acid, m. p. 174°, by directly oxidizing the free fatty acids of the oils which they studied with cold alkaline permanganate solution.

(7) A. Rollet, *Z. physiol. Chem.*, **62**, 410 (1909).

solution was added slowly to the soap solution which was shaken after each addition. After a quarter of an hour when the last drop of permanganate solution was added, sulfur dioxide was passed into it until the precipitate in the flask became white. The precipitate was filtered off and washed until free from acid. It was dried and then extracted with ether. The ether insoluble residue weighed 11.2 g. and was found to melt at 155–160°. After washing several times with hot benzene the compound was found to melt at 160–168°. The solid was then taken up in hot water. Ten hot water extractions were made. Each one of the first eight extractions was 1 liter while each of the last two was 2.5 liters. On cooling the solutions, a white solid precipitated which was separately filtered. Ten fractions were then collected.

TABLE I

FRACTIONS AND THEIR MELTING POINTS

Fractions	M. p., °C.	Fractions	M. p., °C.
1	160–170	6	155–160
2	160–170	7	155–158
3	160–170	8	165–171
4	155–158	9	165–171
5	156–160	10	167–172

The various fractions were combined to form three new fractions. Fractions 1–3 were designated as fraction A; 4–7, fraction B; 8–10, fraction C.

Fraction A was washed with hot benzene and then recrystallized in hot alcohol. A solid melting at 155 to 160° was obtained. It was added to fraction B which was washed with hot benzene. The residue of B was crystallized in hot alcohol and while the solution was still warm a fraction was obtained which melted at 156 to 158°. On reducing the volume of filtrate, a second crop of solid was obtained which melted at 163°. The first crop of B was recrystallized fractionally in hot alcohol and two crops of solid were obtained; the first crop melted at 168–171° and a second crop at 163°. The higher melting portion was added to C fraction and together were washed with hot benzene, and fractionally crystallized in hot alcohol. The solid in the warm solution was filtered off and found to melt sharply at 174°. On reducing the volume of the filtrate a second crop was obtained which melted at 174°.[8]

All the residual filtrates from the various fractional crystallizations were added and reduced in volume and upon cooling a solid compound was obtained which melted at 155–158°. It was subjected to the same fractional crystallization and the same results were obtained. A small amount of residual solid remained melting at 156–158°. This was undoubtedly a mixture of the two sativic acids. When the fraction melting at 163° was recrystallized, its melting point was raised to 164°.

Oxidation of the Regenerated Linolic Acid of Soya Bean Oil.—4.55 grams of the regenerated linolic acid was oxidized as described above with cold alkaline permanganate solution and 1.4 g. of hot water-soluble compound was obtained. The dried compound was extracted with ether and there remained 1.25 g. of ether-insoluble residue which was found to melt at 158–162°. None dissolved in hot benzene. It was fractionally crystallized as above and the first fractional crystallization gave two fractions, one melting at 166–169° (fraction A) and the other at 159–161° (fraction B). Fraction A on fractional crystallization gave fractions melting at 165–168° and at 161–163°. The lower melting fraction was added to B and upon fractional crystallization the mixture gave α-sativic acid, m. p. 164°. The fraction melting at 165–168° was fractionally crystallized also. The solid obtained from the filtration of the warm solution was found to melt sharply at 174°. The residual filtrates of crystallization were added together and reduced in volume. From the solid obtained two sativic acids were isolated, but a small residue melting at 156–158° remained which was undoubtedly a mixture of the two acids. Oxidation was repeated and the same results were obtained.

Free Fatty Acids of Cottonseed Oil.—The free fatty acids of cottonseed oil were prepared in the same way as the free fatty acids of soya bean oil. The oil is from a stock of commercial oil in the Department of Chemistry, University of the Philippines.

Oxidation of the Free Fatty Acids of Cottonseed Oil.—Thirty grams of the dried fatty acids from cottonseed oil was oxidized in the same manner as previously described for the fatty acids of soya bean oil; 6.07 g. of ether insoluble solid was obtained. This solid was extracted thoroughly with hot water. The aqueous extract was allowed to cool down, and from it was obtained 1.66 g. of dried product. This dry material was subjected to fractional crystallization in hot alcohol. The solid which separated from the warm solution was found to melt at 174°. Upon evaporating the filtrate, a second crop was obtained melting at 158–161°. After reducing the volume of the filtrate, a third crop was obtained. It was a very small amount, melting at 158–160°. The two lower fractions were fractionally crystallized together. While the solution was still warm, a fraction of solid was obtained which was found to melt at 164°. A second fraction was obtained melting at 156–158° from which a small quantity of solid melting at 164° was isolated. A small portion melting at 155–158° remained. This was undoubtedly a mixture of the two sativic acids. Oxidation was repeated and the same results were obtained.

Preparation of Linolic Acid Tetrabromide of the Free Fatty Acids of Cottonseed Oil.—Bromination of the dry ethereal solution of 336 g. of the free fatty acids of cottonseed oil was carried out in the same manner as previously described. Crystallization of the solid tetrabromide was done in low boiling petroleum ether. The compound obtained after two recrystallizations melted at 114°. No solid tetrabromide of lower melting point was isolated.

Regenerated Linolic Acid of Cottonseed Oil.—This was prepared as previously described elsewhere in this paper: 34.918 g. of α-linolic acid tetrabromide, m. p. 114°, was the starting material. Digestion on the water-bath was continued for a period of fifty-two hours. Care was exercised in the different operations to avoid loss of material; 16.885 g. of product was obtained. From these figures the percentage yield and purity of product was found to be 97.6%.

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(8) Tsujimoto [*Chem. Rev. Fett- Harz-Ind.*, **18**, 111 (1911)] reported having obtained a tetrahydroxystearic acid from soya bean oil melting at 156–157.5°. This is probably not a pure acid and undoubtedly a mixture of the two sativic acids melting, respectively, at 164 and 174°.

TABLE II

ANALYTICAL DATA[a]

Substance	Sample used, mg.	CO₂, mg.	H₂O, mg.	%, C Found	%, C Calcd.	%, H Found	%, H Calcd.
β-Sativic	5.548[b]	12.553	5.074	61.70	62.1	10.24	10.3
acid	5.647[c]	13.023	5.280	62.85	62.1	10.45	10.3
α-Sativic	5.732[b]	13.110	5.211	62.38	62.1	10.18	10.3
acid	5.395[c]	12.287	4.900	61.70	62.1	10.16	10.3
α-Linolic acid tetrabromide	5.761[d]	7.759	2.753	36.73	36.02	5.35	5.34

[a] The writer wishes to acknowledge his indebtedness to Prof. A. C. Santos of the College of Pharmacy, University of the Philippines, for the micro-analysis.

[b] Analysis of the sativic acids obtained from linolic acid present in the oil of soya bean oil and from the regenerated linolic acid from α-linolic acid tetrabromide of this oil. The sample is a mixture of the corresponding acids obtained from the free acids of the oil and from the regenerated acid.

[c] Analysis of sativic acids from the free fatty acids of cottonseed oil and its regenerated linolic acid. Samples were made in the same manner as with soya bean.

[d] Sample was a mixture of α-linolic acid tetrabromide prepared from the free fatty acid of soya bean oil and its regenerated linolic acid and from the free fatty acids of cottonseed oil. When the sample was recrystallized from a solution of petroleum ether and ordinary ether (1:1), the melting point was raised up to 115–116°. W. C. Smit [*Rec. trav. chim.*, **49**, 539 (1930)] obtained 116–117° as the melting point of the same compound.

Oxidation of the Regenerated Linolic Acid[9] from α-Linolic Acid Tetrabromide of Cottonseed Oil.—5.198 grams of the regenerated linolic acid was oxidized with cold alkaline permanganate solution in the same manner as already described; 3.026 g. of product was obtained. The dried product was washed with ether and then extracted with hot water. The extracted fraction amounted to 1.874 g., m. p. 156–158°. It was washed with hot alcohol. The first fraction of solid obtained while the solution was still warm was found to melt at 174°, second fraction at 156–158°, third fraction at 156–158°. The lower fraction was fractionally recrystallized from hot alcohol. The first crop was found to melt at 163–164°, second crop at 163–164°, third crop at 156–159°. The third crop was undoubtedly a mixture of the two sativic acids. Oxidation was repeated and the same results were obtained.

The purity of the compounds here reported was checked by micro-analysis.

Summary

1. Only one solid tetrabromide, α-linolic acid tetrabromide (m. p. 114°), is obtainable from the direct bromination of the free fatty acids of soya bean and cottonseed oils.

2. Only one solid tetrabromide, α-linolic acid tetrabromide (m. p. 114°), is obtainable from the bromination of the regenerated linolic acid from the α-linolic acid tetrabromide (m. p. 114°) of soya bean oil.

3. Only two tetrahydroxystearic acids, α-sativic acid (m. p. 163°) and β-sativic acid (m. p. 174°) are obtainable from the free fatty acids of soya bean and of cottonseed oils.

4. Only α-sativic acid (m. p. 164°) and β-sativic acid (m. p. 174°) are obtainable from the oxidation with cold alkaline permanganate solution of the regenerated linolic acid from the α-linolic acid tetrabromide prepared from soya bean and cottonseed oils.

MANILA, P. I.

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(9) Nicolet and Cox[2] reported their β-sativic acid as melting at 170° and their α-sativic acid as melting at 153°. Their acids melted appreciably much lower and may still be impure. Meyer and Beer's[2] observation which was doubted by Nicolet and Cox finds strong support in the result of the oxidation of linolic acid actually present in cottonseed oil and of the regenerated linolic acid. S. R. Benson and H. N. Calderwood [THIS JOURNAL, **58**, 523 (1936)] have reported two tetrahydroxystearic acids, m. p. 152 and 173°, which they considered identical to the compounds of Nicolet and Cox. T. G. Green and T. P. Hilditch [*Biochem. J.*, **29**, 1552 (1935)] reported two solid tetrahydroxystearic acids melting at 155 and 173°.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Photoiodination of the Butenes, Propylene and Ethylene at Low Temperatures. Preparation and Photolysis of 1,2-Diiodobutane

BY GEORGE S. FORBES AND ARTHUR F. NELSON

Before undertaking the experiments described below, we had attempted to follow the photobromination of butenes in liquid dichlorodifluoromethane (freon). As the thermal reaction was complete within a few minutes, even at −150°, we substituted iodine monobromide, but the combined bromine still reacted rapidly. The resulting purple solution, stable in the dark, slowly became colorless when irradiated at −150° with a tungsten lamp.[1] Starting next with iodine and excess of butene under the same conditions, the iodine disappeared as before, but reappeared quickly upon exposure to a spark between tungsten steel electrodes.[1] Both the photoiodination of olefins and the photolysis of olefin iodides can thus be studied without interference from competing thermal reactions. At −55° in chloroform, where the solubility of iodine is greater than in freon, the situation was found to be even more favorable.

DeRight and Wiig[2] have reported that iodine reacts rapidly with ethylene in carbon tetrachloride when exposed to a tungsten lamp behind a red filter having maximum transmission at λ 700 mμ. The possibility thus indicated, that the iodination can proceed through excited iodine molecules, without participation of iodine atoms, deserves further investigation.

Materials.—All samples of olefins, ethylene excepted, had been prepared in a state of exceptional purity by Professor G. B. Kistiakowsky and co-workers.[3] We are greatly indebted to them for their coöperation. The bulbs, provided with capillary inner seals and free from air, had been stored at 0°. We distilled each butene in a vacuum into a new container provided with several capillary inner seals, so that successive samples could be withdrawn without introduction of air. The propylene was condensed to a liquid, and the first portion to vaporize was discarded. A sample of commercial ethylene known to be very pure[4] was drawn from a steel cylinder and similarly treated.

Chloroform of "analytical" grade was shaken once with 9 *M* sulfuric acid, and the alcohol extracted by five washings with water. A treatment with aniline eliminated phosgene. The product was distilled from an all-glass Podbielniak still[5] having a 150-cm. column and a spiral of nichrome wire as packing. The reflux ratio exceeded 5, and the range was not over 0.02°.

Iodine of "analytical" grade, stated to be free from cyanogen and 99.97% pure, was resublimed from iodide and preserved in a desiccator without grease.

Apparatus and Procedure.—The reaction cell was a rectangular prism of thin fused quartz 1 × 2 cm. in horizontal cross section and 5 cm. high. It had a cylindrical neck 7 cm. long and 2 cm. in diameter. The hollow ground-glass stopper was surmounted by tubes to admit a small high-speed stirrer and to deliver or pump out gases. The jacket was made from a short Dewar vessel, to the top of which was cemented a cylinder of Pyrex 11 cm. high and 5 cm. in diameter. A rectangular opening was cut in this tube just large enough to admit a closed quartz cell 3 × 7 cm. having plane polished faces 0.5 cm. apart, which served as a double window. The jacket was insulated with cellulose wool, and enclosed in a wooden box having a hole corresponding to the window. The reaction cell behind the window was held at −55 ± 5° by liquid air added at suitable intervals. The outer surface of the double window was kept free from moisture by a current of warm air.

A bulb containing olefin vapor was fused to a gas buret through a three-way stopcock and the intervening space evacuated. A capillary inner seal was broken by a magnetic hammer and enough vapor drawn out over mercury to make 100 cc. of 0.01 *M* solution. By turning the stopcock the vapor was dissolved readily under chloroform at −60° in a 100-cc. flask, and a millimole of iodine was added. The stock solution was stored, transferred and weighed without exposure to actinic light. It is shown below that the olefin iodide formed on standing was without influence upon the results.

The mercury vapor lamp,[6] monochromator and thermopile-galvanometer system[7] have been described. Before and after each photoiodination the linear thermopile was placed successively in three positions 1 mm. apart, close behind the exit slit so that the emerging beam was wholly covered. The sum of the three galvanometer deflections $\Sigma\Delta$ equaled kL, where L was the energy flux. Fifteen times during the research, uranyl oxalate was exposed in the reaction cell behind the double window, intercepting the whole of the beam. $\Sigma\Delta$ was redetermined before and after each exposure. When L had been found from the oxalate decomposed and the time, k was evaluated. Reflection corrections canceled out, quite nearly. Chatelet's extinction coefficients, ϵ, for iodine in chloroform at 18° were used at −55° without change.[8] The contraction of the chloroform solutions, 20 to −55°, tended to counteract a possible decrease in ϵ over the same range.

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(1) Forbes and Nelson, THIS JOURNAL, **58**, 182 (1936).

(2) DeRight and Wiig, *ibid.*, **58**, 693 (1936).

(3) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935).

(4) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 65 (1935).

(5) Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 119 (1930).

(6) Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

(7) Forbes, Heidt and Boissonnas, *ibid.*, **54**, 960 (1932).

(8) Chatelet, *Ann. chim.*, [11] **2**, 26 (1934).

On this basis less than 2% of incident light was ordinarily transmitted and the indicated correction factor never exceeded 1.07.

The photolyzed solution, also an unexposed sample weighed with equal care, were shaken separately in the dark with excess of 0.01 *N* thiosulfate. After drawing off the decolorized chloroform solutions, the water solutions were titrated back with standard iodine. The olefin iodides in the chloroform layers liberated no visible iodine in the dark at room temperature in twelve hours, but in diffused daylight a purple color appeared within a few minutes.

Data on Quantum Yields.—Table I gives quantuum yields, ϕ in terms of molecules of iodine reacting with olefin in light of λλ 436 and 546 mμ. An initial series of *cis*-butene, yielding very high values, could not be repeated, and was rejected. Initial concentrations were uniformly 0.01 *M* in olefin and in iodine. Experiments not marked (*b*) employed stock solutions described above containing some olefin iodide. Experiments (*b*) were started by weighing finely divided

TABLE I

λ 436 mμ				λ 546 mμ			
t, sec.	Quanta per sec.	Molecules of iodine	Quantum yield	*t*, sec.	Quanta per sec.	Molecules of iodine	Qauntum yield
			BUTENE-1 AND IODINE				
1800	1.17×10^{15}	4.47×10^{18}	2.09^a	1920	2.46×10^{15}	3.28×10^{18}	0.69
1800	1.18×10^{15}	4.37×10^{18}	2.04^a	1800	2.58×10^{15}	3.29×10^{18}	.71
1800	1.53×10^{15}	6.18×10^{18}	2.27	1800	2.62×10^{15}	3.34×10^{18}	.71
1800	1.54×10^{15}	5.64×10^{18}	2.12	1800	2.16×10^{15}	3.55×10^{18}	.92
1800	1.30×10^{15}	5.49×10^{18}	2.35	1800	1.99×10^{15}	3.36×10^{18}	.94
1800	1.31×10^{15}	4.58×10^{18}	1.94^b			Average	0.80
1800	1.35×10^{15}	5.67×10^{18}	2.32^b				
3600	1.46×10^{15}	9.33×10^{18}	1.78				
3600	1.46×10^{15}	9.49×10^{18}	1.81				
		Average	2.08				
			trans-Butene and Iodine				
3600	1.35×10^{15}	2.99×10^{18}	0.61	1800	2.55×10^{15}	1.68×10^{18}	0.37
3600	1.29×10^{15}	3.42×10^{18}	.73	1800	2.58×10^{15}	1.65×10^{18}	.36
3600	1.49×10^{15}	2.72×10^{18}	.51	1800	2.57×10^{15}	1.67×10^{18}	.36
3600	1.50×10^{15}	3.48×10^{18}	.65	1800	2.25×10^{15}	1.62×10^{18}	.40
		Average	0.63	1800	2.16×10^{15}	1.41×10^{18}	.36
						Average	0.37
			i-Butene and Iodine				
3600	1.60×10^{15}	2.66×10^{18}	0.52	3600	2.58×10^{15}	4.72×10^{18}	0.51
3600	1.59×10^{15}	2.85×10^{18}	.56	3600	2.66×10^{15}	3.89×10^{18}	.41
3600	1.62×10^{15}	2.98×10^{18}	.57	3600	2.88×10^{15}	3.88×10^{18}	.37
1800	1.52×10^{15}	1.64×10^{18}	.66	3600	2.84×10^{15}	3.58×10^{18}	.35
1800	1.57×10^{15}	1.42×10^{18}	.57			Average	0.41
		Average	0.58				
			cis-Butene and Iodine				
1800	1.62×10^{15}	7.80×10^{18}	2.67	1800	3.10×10^{15}	5.86×10^{18}	1.05
1800	1.57×10^{15}	6.96×10^{18}	2.46	1800	3.15×10^{15}	6.30×10^{18}	1.11
1800	1.56×10^{15}	6.42×10^{18}	2.28	1800	3.17×10^{15}	4.91×10^{18}	0.86
1800	1.55×10^{15}	6.73×10^{18}	2.41	1800	3.24×10^{15}	7.06×10^{18}	1.21
		Average	2.48			Average	1.06
			Propylene and Iodine				
1800	1.26×10^{15}	5.73×10^{18}	2.51^a	1800	1.96×10^{15}	2.72×10^{18}	0.77^a
1800	1.11×10^{15}	5.52×10^{18}	2.76^a	1800	1.91×10^{15}	3.71×10^{18}	1.08^a
1800	1.54×10^{15}	7.70×10^{18}	2.89	1800	2.18×10^{15}	3.67×10^{18}	0.94
1800	1.52×10^{15}	8.75×10^{18}	3.08	1800	2.23×10^{15}	3.74×10^{18}	.93
1800	1.53×10^{15}	9.07×10^{18}	3.30	1800	2.14×10^{15}	3.53×10^{18}	.92
1800	1.52×10^{15}	8.10×10^{18}	2.82	1800	2.02×10^{15}	3.35×10^{18}	.92
1800	1.31×10^{15}	6.67×10^{18}	2.84^c				
1800	1.33×10^{15}	5.25×10^{18}	2.19^c			Average	0.93
		Average	2.80				

iodine into olefin solution in the cell at −60° in the dark, so that no olefin iodide was present at the start. As such a variation in procedure had no visible effect upon ϕ, it was concluded that the iodine-sensitized photodecomposition of the olefin iodides was negligible at −60°. According to Schumacher and Wiig[9] this reaction, rapid at 100°, becomes unimportant at 20°, so that our finding is consistent with theirs. Olefin iodide does not itself absorb light perceptibly unless $\lambda < 360$ mμ.[10]

Oxygen reacts photochemically with methylene iodide[11] and accelerates the photolysis of iodoform.[12] Emschwiller[13] reports that in ultraviolet light CH_3CHI_2 and CH_2CI_2 react completely with atmospheric oxygen, while $(CHI)_2$ and $(CH_2I)_2$ are unaffected. Though we believed that our addition product was symmetrical[14] the effect of oxygen on certain photohalogenations[15] suggested caution. DeRight and Wiig froze, pumped out and melted their solutions, of ethylene and iodine, twice before exposing them to red light. In experiments marked (*c*) we carried out the above cycle three times; the solution was photolyzed in a vacuum and shaking was substituted for stirring. In experiments marked (*a*) oxygen was partially removed by bubbling gaseous freon through the cell during photolysis. The results appeared to be the same whether oxygen was removed almost completely, partially, or not at all.

Professor E. O. Wiig kindly lent his approval to our suggestion that we compare ethylene with propylene and butenes. Our procedure remained unchanged. To our surprise the total reaction after one hour scarcely exceeded the probable error of analysis. With ethylene iodide absent at the start, but without exclusion of air

λ 436 ϕ = 0.07 0.10
λ 546 ϕ = 0.00 0.03

Starting with a solution containing ethylene iodide, and without exclusion of air

λ 436 small increase in free iodine
λ 546 ϕ = 0.06 0.06 0.04
λ 577 ϕ < 0.01
λ 644 ϕ (red line of cadmium spark[16,17]) ϕ = 0.01

To decide whether the low value of ϕ at λ 644 was peculiar to the ethylene, *cis*-butene was substituted, with similar results

λ 644 ϕ = 0.01 0.02

To correlate our single experiment at λ 644 with those of DeRight and Wiig, we determined the spectral transmission of a sheet of red cellophane, and the spectral energy distribution of a 200-watt tungsten lamp, including all the infra-red. Using these data together with the energy consumption of two such lamps, and the dimensions of the apparatus, we calculated that 3.3×10^7 ergs/sec. of radiation λ 800 to 546 mμ, entered our reaction mixture. In two hours about 2.0×10^{19} molecules of iodine disappeared.

Two experiments were performed without removal of oxygen: at −55 ± 5°, $\phi = 0.007$; at 25°, $\phi = 0.004$. Also two experiments at −55 ± 5°, after removal of air by freezing, pumping and melting three times, gave 0.006 and 0.005, respectively. As DeRight and Wiig state that ethylene and iodine react rapidly in red light, it is evident that their light flux was considerably greater than ours.

The reaction scheme of Schumacher[18] has proved adequate for the discussion of previous results, photochemical as well as thermal, at room temperature.

$$I_2 + h\nu \longrightarrow I + I \quad (1)$$
$$I + C_2H_4 \longrightarrow C_2H_4I \quad (2)$$
$$C_2H_4I \longrightarrow C_2H_4 + I \quad (3)$$
$$C_2H_4I + I_2 \longrightarrow C_2H_4I_2 + I \quad (4)$$

It permits ϕ to exceed 2 (*e. g.*, *cis*-butene), and is not incompatible with small values of ϕ (*e. g.*, ethylene). We could discover no correlation between ϕ (at λ 546 and −55.0°) and $\Delta F°$ at 25° for the olefins[19] as a whole. Apparently, then, ϕ does not depend upon the stability of the olefin as a whole, as it would if stability influenced the position of equilibrium in a partial reaction involving olefin. The same holds for ϕ in its relation to the stabilities of the ethylenic linkages considered separately.[20]

To test further the adequacy of Schumacher's reaction scheme at −55°, concentrations and light intensities were varied. Owing to the labor involved, *cis*-butene alone was thus investigated. Little variation in iodine concentration was practicable. A 0.01-molar solution at −55° is nearly saturated, while light transmission and

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[9] Schumacher and Wiig, *Z. physik. Chem.*, **B11**, 47 (1930).
[10] *Cf.* DeRight and Wiig, THIS JOURNAL, **57**, 2412 (1935).
[11] Gregory and Style, *Trans. Faraday Soc.*, **32**, 724 (1936).
[12] Gibson and Iredale, *ibid.*, **32**, 571 (1936).
[13] Emschwiller, *Compt. rend.*, **199**, 854 (1934).
[14] *Cf.* A. Sherman, Quimby and Sutherland, *J. Chem. Phys.*, **4**, 732 (1936).
[15] *Cf.* Willard and Daniels, THIS JOURNAL, **57**, 2240 (1935).
[16] Wiig and Kistiakowsky, *ibid.*, **54**, 1807 (1932).
[17] Forbes and Heidt, *ibid.*, **56**, 1671 (1934).
[18] Schumacher, *ibid.*, **52**, 3132 (1930).
[19] Values from Parks, *Chem. Rev.*, **18**, 325 (1936).
[20] Values from Kistiakowsky and co-workers, refs. 3, 4.

analytical errors impair results when $c < 0.005$. Experimental data appear in the first three columns of Table II, the unit of volume being one cc. In the fourth is the observed rate of disappearance of iodine in moles per second, and in the fifth the widely fluctuating rate constant calculated by inserting the photochemical formation of iodine ions into Schumacher's scheme. At −55° the expression $d[BI_2]/dt\ [B][I_2]L_a$ given in the last column is much more nearly constant.

Table II

$[B] \times 10^6$	$[I_2] \times 10^6$	L_a (Einsteins/cc.) $\times 10^{10}$	$-\frac{d[I_2]}{dt} \times 10^{10}$	$\frac{d[BI_2]}{dt} / [B]\sqrt{L_a}$	$\frac{d[BI_2]}{dt} / [B][I_2]L_a \times 10^{-10}$
4.57	9.62	1.88	2.18	3.48	2.61
4.55	9.60	1.98	2.14	3.35	2.47
4.54	9.59	2.18	1.99	2.94	2.10
6.67	10.18	1.54	3.88	4.70	3.71
6.74	10.25	1.50	3.32	4.02	3.20
6.67	10.18	1.45	3.88	4.84	3.94
8.12	7.64	2.68	7.15	5.38	4.30
8.09	7.61	2.60	6.40	4.90	4.00
8.05	7.57	2.58	5.88	4.55	3.74
8.00	7.52	2.56	6.17	4.81	4.00
35.35	5.60	2.06	16.75	3.48	4.10
35.18	5.43	1.95	15.44	3.13	4.15
35.04	5.29	2.08	17.23	3.41	4.47
10.00	4.52	1.12	1.57	1.49	3.10
9.90	4.42	1.12	1.67	1.58	3.40
9.88	4.40	1.10	1.72	1.64	3.60
9.40	8.86	0.328	0.86	1.58	3.14
9.33	8.79	.259	.52	1.11	2.45
8.99	6.49	.756	1.14	1.11	2.59
8.96	6.46	.754	1.23	1.20	2.82
19.38	8.63	.292	1.17	1.11	2.40
19.52	8.78	.276	1.19	1.17	2.51
50.66	7.64	.209	1.99	0.85	2.41
49.60	6.60	.178	1.89	0.88	3.24
49.13	6.13	1.19	10.21	1.90	2.84
49.10	6.00	1.23	9.97	1.84	2.75

Preparation and Photolysis of 1,2-Diiodobutane.—A solution of iodine with excess of butene-1 in freon at −70° was illuminated by two gas-filled tungsten lamps through liter beakers filled with water and serving as lenses until the solution became colorless. The freon was evaporated under reduced pressure below its boiling point, −29.8°, carrying off the excess of butene (b. p. −6°). The white crystals, only about 10 mg. in weight, could not be purified readily by recrystallization, but were believed to be mainly the symmetrical compound.[14] After drying below −25° for several hours, the melting point was −15 ± 1°; the oily liquid was stable at −15° in the dark for some time, but iodine was liberated promptly upon exposure to diffused daylight. A microanalysis of the compound was performed in Converse Laboratory: found 15.56 and 16.49% of C, also 2.84 and 2.94% of H. Calculated for $C_4H_8I_2$, 15.48% of C and 2.60% of H.

We prepared 2,3-diiodobutane in similar fashion from butene-2 (*trans*) also as a white solid. This melted at −11 ± 2° with immediate decomposition, so that attempts at analysis were unsuccessful.

The quantum yield for photolysis of 1,2-diiodobutane in light of λ 254 was determined, using a special argon-filled quartz mercury vapor lamp ("Fluorolight"). As we found 77% of the whole to be resonance radiation,[21] we dispensed with the monochromator. The solution of 1,2-diiodobutane, prepared as above, was slightly purple at the start. The quantum yields appear in Table III under the assumption that diiodobutane absorbed all the resonance radiation. DeRight and Wiig[10] found that ethylene iodide began to absorb at λ 360 and absorbed strongly at λ 313. No allowance was made for absorption by the iodine, since at its mean concentration it could have absorbed only 12% of the incident light even if the strongly absorbing diiodobutane had been absent.

Table III

Quantum Yields of Photodecomposition of 1,2-Diiodobutane

T, °C.	*t*, sec.	Quanta per sec. $\times 10^{-14}$	Molecules decomposed $\times 10^{-18}$	Quantum yield
−55	3600	10.6	2.7	0.7
−55	3600	10.1	2.4	.65
−55	3600	12.2	3.5	.75
−20	3600	12.1	4.1	.95
−20	3600	11.4	4.3	1.05
24	2400	11.4	3.1	1.15
25	2400	11.5	3.1	1.15
25	3600	12.6	4.9	1.1

DeRight and Wiig[10] (p. 2414) have reported for ethylene iodide at room temperature ϕ = 0.71, 0.74, 0.75, 0.81, 0.81. We calculate 1.06 as the ten-degree temperature coefficient from ϕ at −55 and at 25°. From ϕ at −55 and −20° we find 1.08.

We are indebted to the du Pont Fund of the Division of Chemistry for a part of the apparatus used in this investigation.

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[21] *Cf.* W. G. and P. A. Leighton, *J. Chem. Ed.*, **12**, 139 (1935).

Summary

The four butenes, propylene and ethylene, all exceptionally pure, were quantitatively photoiodinated in chloroform at −55° in light of λλ 436, 546 and in two cases 644 mμ. Competing thermal reactions were paralyzed.

The quantum yields for the different olefins at −55° (concentrations and light intensity being the same) vary as much as fortyfold, due perhaps to a difference in the activation energy of a secondary thermal reaction common to all the photoiodinations.

Quantum yields at −55° fall off with decreasing frequency to a value of the order of 0.01 at λ 644 mμ.

The thermal reaction scheme of Schumacher does not harmonize with the photochemical results at −55°. The rate of photoiodination is more nearly in proportion to concentration of olefin and of iodine and to light intensity.

At low temperatures diiodobutane (presumably the 1,2-isomer) was prepared as a white solid in a state of reasonable purity, and photolyzed at −60, −20 and +25°. The quantum yield at 25° is nearly the same as that for symmetrical ethylene iodide.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 8, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Adsorption and Decomposition of Carbon Monoxide on Zinc Oxide Catalysts

BY ROBERT L. BURWELL, JR., AND HUGH S. TAYLOR

The results of an investigation into the rate of the activated adsorption of hydrogen at constant pressure on zinc oxide have been reported by Taylor and Strother.[1] It appeared desirable to extend this work by studying the rate of the activated adsorption of carbon monoxide on the same catalyst.

Experimental

Accordingly the technique and the apparatus of Taylor and Strother were employed. Zinc oxide was prepared in the manner described in their communication. Carbon monoxide was prepared by dropping formic acid into hot sulfuric acid. The effluent gas was passed successively over copper wool heated to 450°, soda lime, calcium chloride and phosphorus pentoxide.

The observed rates of adsorption fell off progressively with an accompanying change in color of the adsorbents from pure white to gray. The results of typical rate determinations are listed in Table I.

TABLE I

RATES OF ADSORPTION OF CARBON MONOXIDE ON 22.7 G. OF ZINC OXIDE, PREPARATION 3C, AT A PRESSURE OF ONE ATMOSPHERE

Adsorption in cc., N. T. P.

Time, min.	2	4	8	12	20	40	60	100
Run 6 184°	2.1	2.75	3.45	4.0	4.7	5.9	6.75	7.9
Run 7 218°	3.45	4.45	5.7	6.55	7.85	9.8	11.1	12.9
Run 8 184°	1.9	2.45	3.2	3.65	4.35	5.4	6.1	7.15

Twenty-one runs in all were made on preparation 3C at the two temperatures listed in Table I. They were similar to the ones in the table and showed a progressive deactivation of the catalyst surface. Similar results were obtained on another zinc oxide sample, preparation 3B.

Hydrogen was then substituted for carbon monoxide and a number of rates of adsorption of that gas were determined at temperatures of 184 and 218°. After a few runs it was observed that the initial white color of the adsorbent had been regenerated. Adsorptions of hydrogen were very much greater and more rapid during the first few runs than in the subsequent ones.

These phenomena may be explained plausibly by the assumption that carbon monoxide is decomposed on the catalyst surface in accordance with the equation

$$2CO \longrightarrow C + CO_2$$

On admission of hydrogen, the deposited carbon is assumed to react to produce methane. Such a mechanism may account for the small amount of methane produced by similar catalysts in the methanol synthesis.[2] The decomposition of carbon monoxide corresponds to a considerable decrease in the free energy of the system at the temperatures under consideration.[3] Such a decomposition of carbon monoxide has been reported for other oxide catalysts.[4]

To test this hypothesis, an apparatus was constructed which permitted the passage of carbon monoxide over copper wool at a temperature of 400°, then successively through two spiral bubbling bottles containing solutions of barium hydroxide (no turbidity ever appeared in the second bottle), a tube containing calcium chloride and one containing phosphorus pentoxide. The gas passed thence through a tube containing 15 g. of zinc oxide. The off gas was passed through a bubbling tube into which a solution of barium hydroxide could be directly filtered and thence through a bubbling bottle containing barium hydroxide.

(1) Tank nitrogen purified in a manner similar to that of carbon monoxide, was passed over the sample of zinc

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(1) Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

(2) Rideal–Taylor, "Catalysis in Theory and Practice," The Macmillan Co., London, 1926, p. 257 *et seq.*

(3) Lewis and Randall, "Thermodynamics," 1923, p. 573.

(4) H. Göthel in "Grenzflächen-katalyse," by M. Kroger, S. Hirzel, Leipzig, 1933, p. 104.

oxide maintained at a temperature of 425–450° for twenty hours at a rate of 2 to 5 cc. per minute. The catalyst was cooled to room temperature and the apparatus was flushed out with carbon monoxide. The temperature of the catalyst was elevated and maintained at 184° by means of an aniline vapor-bath. Barium hydroxide solution was inserted in the test bubbler. Turbidity appeared in ninety minutes.

The catalyst was cooled to 20° and the system was flushed out with nitrogen. The temperature was elevated gradually by means of a furnace. Turbidity appeared in a fresh barium hydroxide solution at 175°. Larger amounts of barium carbonate appeared as the temperature rose. The bulk of the precipitate formed between 340 and 400°.

The nitrogen passage was continued at a rate of 4 cc. per minute. After fourteen hours with the temperature of the catalyst maintained at 435°, no turbidity appeared in fresh barium hydroxide solution in two hours.

(2) The catalyst was cooled to room temperature and carbon monoxide passed through the system for twenty hours. No turbidity was evident in the test bubbler. On elevating the temperature to 184° faint turbidity appeared only after twelve hours.

Nitrogen was substituted for carbon monoxide and the temperature of the catalyst elevated in the same fashion as described in (1). Similar results were obtained. After nitrogen passage for four hours over the catalyst maintained at 420°, new barium hydroxide was inserted in the test bubbler. The temperature of the catalyst and the rate of nitrogen passage were continued. No turbidity was evident after twelve hours.

(3) The sequence of operations described in (2) was repeated. Results were similar save that forty-eight hours were required for the appearance of a faint turbidity at 184°.

(4) Carbon monoxide was passed through the system to displace the nitrogen with the temperature of the catalyst held at 300°. With fresh barium hydroxide solution in the test bubbler, turbidity appeared in half an hour. With the temperature of the catalyst at 370°, fresh barium hydroxide solution gave an immediate precipitate.

(5) During these experiments the catalyst had become markedly gray-brown. Hydrogen was passed over the catalyst for ten hours at 385°. The color of the catalyst lightened considerably and appeared a light gray.

Discussion

The experiments described in (1) to (5) demonstrate that carbon monoxide is in some degree decomposed to carbon dioxide in passage over active zinc oxide catalysts at temperatures above 184°. Only a small part of this carbon dioxide could be ascribed to an oxidation of carbon monoxide by zinc oxide.[5] In the course of the work described in (1) to (5) and especially in (4) large volumes of carbon dioxide were formed. Had such a volume of carbon dioxide been produced by the reduction of zinc oxide, a corresponding amount of zinc should have sublimed into the off tube. No such quantity was observed. It is further impossible to account by such an assumption for the effect of hydrogen in restoring the color of the catalyst.

The fall in catalytic activity of the zinc oxide surface as exemplified by the increasing times required to produce turbidity at a temperature of 184° may be presumed partially at least to have resulted from a covering of the "active spots" by carbon.

The slow reaction in the adsorption process cannot, however, have been the decomposition of carbon monoxide with subsequent adsorption of the carbon dioxide so produced. For were this true, zinc oxide could not act as a catalyst in the methanol synthesis. Further, were all of the adsorbed carbon monoxide to have been decomposed, one would expect all of the active surface to have been covered with carbon in the course of several runs, whereas the adsorption was still 40% of its initial value after twenty-one runs. From the excess hydrogen adsorbed in the first couple of runs after its substitution for carbon monoxide one may estimate that no more than about 15% of the carbon monoxide adsorbed during the twenty-one runs could have been decomposed.

Though it is clear that the observed rates of adsorption refer essentially to the activated adsorption of carbon monoxide on zinc oxide, the disturbing influence of the decomposition reaction renders unreliable any calculation of activation energies for the process. However, the activation energies appear somewhat higher than those reported by Taylor and Strother[1] for the adsorption of hydrogen on the same catalyst.

Garner and Maggs[6] have reported recently their inability to detect any activated adsorption of carbon monoxide on zinc oxide at temperatures up to 313° A. They conclude: "The absence of a discontinuity" (in the adsorption isobar) "in the case of carbon monoxide on zinc oxide supports the contention that such discontinuities do not occur in the absence of capillary flow." It is difficult to understand how the mere presence or absence of activated adsorption can decide which of the various theories of the mechanism of activated adsorption is correct. In any case had Garner proceeded to measurements at higher temperatures, he would have discovered the presence of activated adsorption.

In 1931, Taylor[7] pointed out that certain steps

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[5] Burwell and Taylor, THIS JOURNAL, 58, 1753 (1936).

[6] Garner and Maggs, *Trans. Faraday Soc.*, 32, 1774 (1936).

[7] Taylor, THIS JOURNAL, 53, 578 (1931).

in many sorption processes must involve activation energies frequently of a considerable magnitude. It was at first thought that the rate determining step was the approach of the gas molecule to the surface. That such could not universally be true was indicated by the work of Pace and Taylor[8] and by that of Kohlschuetter[9] demonstrating that, at a pressure of one atmosphere and within limited temperature ranges, hydrogen and deuterium were adsorbed with the same velocity on zinc chromite, nickel, and chromium oxide gel, and by the work of Burwell and Taylor[10] on the effect of pressure on the rate of the activated adsorption of hydrogen on chromium oxide gel.

Garner[6,11] has recently reiterated the contention that in general the slow process in activated adsorption is the "diffusion" of the gas down capillaries from an initial rapid adsorption, a view that derives initially from Ward.[12] The application of the term "diffusion" to the suggested mechanism is misleading since whereas true diffusion increases with the temperature as $\sqrt{T}$, the hypothesized "diffusion" of Ward and Garner increases very much more rapidly. Lennard-Jones[13] has shown that to account for the large temperature coefficient it is necessary to assume that before diffusion can take place, a molecule must be raised from its initially adsorbed state to a higher energy level. While the process proposed by Lennard-Jones may occur in some instances, it cannot be a general one. For this hypothesis requires that the amount of adsorption be initially proportional to the square root of the time, a relation which rarely fits time–adsorption data. Further, such a picture is unable to account for the identity of the rates of adsorption of hydrogen and deuterium on the catalysts mentioned previously.

Summary

Experiments are reported which indicate that: (1) carbon monoxide is decomposed in the sense of the equation, $2CO \longrightarrow C + CO_2$, on surfaces of zinc oxide at temperatures above 184°. (2) Carbon deposited on the catalyst is removed by hydrogen at temperatures of 184° and above, presumably as methane.

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[8] Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

[9] Kohlschuetter, *Z. physik. Chem.*, **A170**, 300 (1934).

[10] Burwell and Taylor, THIS JOURNAL, **58**, 697 (1936).

[11] Garner and Veal, *J. Chem. Soc.*, 1487 (1935).

[12] Ward, *Proc. Roy. Soc.* (London), **A133**, 522 (1931).

[13] Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1932).

PRINCETON, N. J. RECEIVED OCTOBER 26, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Calculation of Second Order Reaction Velocity Constants

BY JULIAN M. STURTEVANT

Introduction.—In the application of physical methods to the determination of reaction velocities the observed quantity is usually a property of the reacting system which varies linearly with the concentrations of the reactants and products. To evaluate the two constants involved in this linear relation it is, in general, necessary to obtain the values of the observed property at the start and finish of the reaction. In many cases it is impossible to obtain these values reliably; for example, if the reaction is being followed by observation of the temperature changes resulting from the heat evolved in the system under adiabatic conditions, there would obviously be serious experimental difficulties in obtaining the temperature of the system at the completion of the reaction.

A method of calculation which eliminates these difficulties in certain cases has been described by Roseveare.[1] This method involves the analytical or graphical elimination of the "infinity reading." As pointed out by Roseveare, this method has the further advantage of not giving undue weight to the infinity reading in cases where it cannot be obtained with any greater accuracy than the other readings. Roseveare discussed the application of the method to first order reactions and to second order reactions in which the initial concentrations of the reactants are equal.

In extending the method to more complicated reactions one finds that the algebraic treatment becomes excessively cumbersome. In the present communication it will be shown that these difficulties are avoided by a simple application of the methods of projective geometry. In the course of this treatment there will be developed a very easily applied test as to whether a given set of

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[1] Roseveare, THIS JOURNAL, **53**, 1651 (1931).

experimental data follows a certain kinetic equation.

Kinetic Equation.—The general equations[2] for several types of reactions may be written in the form

$$kt = \ln c\,\frac{a - x}{b - x} \qquad (1)$$

where k is proportional to the velocity constant, $a \neq b$, c are constants, and x is the extent of the reaction at time t, or some quantity varying linearly with it. If $x = x_0$ at $t = 0$, $c = (b - x_0)/(a - x_0)$. Included among the types of reactions following this equation are bimolecular irreversible and reversible reactions (reverse reaction also bimolecular) in which the concentrations of the reactants are not equal, autocatalytic bimolecular irreversible reactions, and trimolecular irreversible reactions in which one reactant is a catalyst or its concentration is much greater than those of the other two reactants.

In equation (1) the constants a, b, c will in general involve the initial concentrations of the reactants, the equilibrium constant for the reaction if it is reversible, and x_0 and x_∞, the value of x at $t = \infty$. Our problem is to determine k from the observed values of x without using x_0, x_∞.

Determination of *k*, *a*, *b*, *c*.—Proceeding in a manner analogous to that recommended by Roseveare[1] for first order reactions we suppose readings x_1, x_2, x_3, x_4 are taken at t, $t + \Delta t$, $t + 2\Delta t$, $t + 3\Delta t$, readings x_1', x_2', x_3', x_4' at t', $t' + \Delta t$, $t' + 2\Delta t$, $t' + 3\Delta t$, and so on. Substitution of these values in equation (1) and subtraction gives a series of simultaneous equations

$$\frac{(a - x_2)(b - x_1)}{(a - x_1)(b - x_2)} = \frac{(a - x_3)(b - x_2)}{(a - x_2)(b - x_3)} = \frac{(a - x_4)(b - x_3)}{(a - x_3)(b - x_4)} = \frac{(a - x_2')(b - x_1')}{(a - x_1')(b - x_2')} = \ldots \equiv \alpha = \text{constant} \qquad (2)$$

from which a, b may be determined in terms of x_1, x_2, ... Substitution of these values in any of the equations

$$k\,\Delta t = \ln \frac{(a - x_2)(b - x_1)}{(a - x_1)(b - x_2)} = \ldots = \ln \alpha \qquad (3)$$

would enable us to obtain k. However, treatment of equations (2) by the usual algebraic methods leads immediately to cumbersome equations the simplification of which is difficult.

The observation[3] that the quantity $\frac{a - x_2}{b - x_2}\Big/\frac{a - x_1}{b - x_1}$ is the so-called anharmonic ratio[4] or cross-ratio of the range of points a, b, x_2, x_1 suggests that the methods of projective geometry may find application here.

The anharmonic ratio of a range of four collinear points, P_1, P_2, P_3, P_4 may be defined as

$$[P_1P_2P_3P_4] = \frac{P_1 - P_3}{P_2 - P_3} \times \frac{P_2 - P_4}{P_1 - P_4} \qquad (4)$$

In this notation equations (2) become

$$[abx_2x_1] = [abx_3x_2] = [abx_4x_3] = [abx_2'x_1'] = \ldots = \alpha \qquad (5)$$

If we consider a, b as fixed points on a line the position of any other point P_i on the line is fixed by the ratio

$$\alpha_i = (a - P_i)/(b - P_i) \qquad (6)$$

It is easily shown that $[abP_iP_j] = \alpha_i/\alpha_j$, so that equations (5) become

$$\alpha = \frac{\alpha_2}{\alpha_1} = \frac{\alpha_3}{\alpha_2} = \frac{\alpha_4}{\alpha_3} = \frac{\alpha_2'}{\alpha_1'} = \ldots \qquad (7)$$

Using equations (6) and (7) and the definition of the anharmonic ratio we readily find that

$$[ax_1x_2x_3] = [ax_2x_3x_4] = [ax_1'x'x_3'] = \ldots = 1 + \alpha^{-1} \qquad (8)$$

$$[bx_1x_2x_3] = [bx_2x_3x_4] = [bx_1'x_2'x_3'] = \ldots = 1 + \alpha \qquad (9)$$

and

$$-[x_3x_1x_2x_4] = -[x_3'x_1'x_2'x_4'] = \ldots = \alpha + 1 + \alpha^{-1} = \text{constant} \equiv A \qquad (10)$$

Equation (10) gives us a simple method for calculating k and a criterion as to whether experimental data follow equation (1). Evidently

$$\alpha = \frac{A - 1}{2} \pm \sqrt{\left(\frac{A - 1}{2}\right)^2 - 1} \qquad (11)$$

where

$$A = \frac{(x_3 - x_2)(x_4 - x_1)}{(x_2 - x_1)(x_4 - x_3)} = \frac{(x_3' - x_2')(x_4' - x_1')}{(x_2' - x_1')(x_4' - x_2')} = \ldots > 3 \qquad (12)$$

so that

$$k\,\Delta t = \ln \alpha = \cosh^{-1}((A - 1)/2) \qquad (13)$$

According to equation (12) data which conform to equation (1) should give a constant value of $A > 3$. This test of the conformity of the data requires no knowledge of the concentrations of the reactants and, as stated before, x may be any quantity varying linearly with the concentrations.

From the value of A the constant k may be calculated. The determination of the sign of the radical in equation (11) offers no difficulty, since

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(2) See the summary of equations, Vol. II, in "*Treatise on Physical Chemistry*," edited by H. S. Taylor, D. Van Nostrand Company, New York, 1931, p. 960.

(3) The author is indebted to Professor H. T. Engstrom of the Department of Mathematics for suggesting the use of projective geometry in this problem.

(4) See, for example, "*The Principles of Projective Geometry*," by J. L. S. Hatton, Cambridge University Press, 1913.

the quantity with the plus sign is the reciprocal of that with the minus sign, and one can readily tell whether $k\Delta t$ should be positive or negative. Unfortunately there will be a serious magnification of errors in cases where A is not much larger than 3, since α varies rapidly with A in this vicinity. Means of avoiding this difficulty are described below. In passing it may be pointed out that expansion of the inverse hyperbolic cosine gives the expression

$$k^2\Delta t^2 = (A - 3)\,[1 - (A - 3)/12 + \ldots] \quad (14)$$

In cases where α may be calculated accurately by this method we may evaluate a, b from equations (8) and (9)

$$a = \frac{\alpha x_1(x_3 - x_2) - x_3(x_2 - x_1)}{\alpha(x_3 - x_2) - (x_2 - x_1)}, \qquad b = \frac{x_1(x_3 - x_2) - \alpha x_3(x_2 - x_1)}{(x_3 - x_2) - \alpha(x_2 - x_1)} \quad (15)$$

and similar equations involving the other x's. Also c is readily obtained from equation (1)

$$c = \frac{\alpha(x_3 - x_2) - (x_2 - x_1)}{(x_2 - x_2) - \alpha(x_2 - x_1)}\,\alpha^{(t + \Delta t)/\Delta t} \quad (16)$$

In such cases it would thus be possible in general to evaluate one of the initial concentrations or the equilibrium constant from the observed data, in addition to x_0 and x_∞.

The magnification of errors involved in equation (11) in many cases may be avoided by using the experimentally determined values for the initial concentrations (and the equilibrium constant if the reaction is reversible). In general it will be possible to calculate one of the quantities a, b, c (or some combination of them) accurately from the known initial concentrations. Then one merely has to calculate α from the appropriate one of equations (15) and (16) (or the appropriate combination of them). If c is the constant whose value is considered as being accurately known, α will have to be calculated by successive approximations, the first of which may be obtained from equation (11).

In connection with this method of calculation two things may be pointed out. It is only necessary to have three readings x_1, x_2, x_3 in each set so that the time interval Δt may be taken larger. Also, in cases where α is very sensitive to the value of A, there will be a corresponding sensitivity of c and either a or b to α, so that the value of α may be obtained accurately.

It may be emphasized again that this extension of Roseveare's method of calculation will be of greatest importance in cases where it is physically impossible to obtain initial or final values of x. For example, in the determination of reaction velocities by following the rate of heat evolution[5] it will evidently be out of the question to observe directly either the value of x_0 because of the heat of mixing, or of x_∞ because of calorimetric difficulties. On the other hand, the concentrations of the reactants at $t = 0$ will be known from the make-up of the reacting solution with an accuracy great enough to warrant their use in the manner described above. As a matter of fact, if it is possible to make the original observations at uniform time intervals, the present method of calculation may result in a considerable saving of time even in cases where initial and final values of x can be obtained with good accuracy, both in enabling one to cease observations before the reaction is finished and in simplifying the calculations.

Example.—The data of Harned and Pfanstiel[6] for the bimolecular reversible hydrolysis of ethyl acetate catalyzed by acids have been treated by the above method. These data follow equation (1) very closely when calculated in the usual way.

In this particular case of a bimolecular reversible reaction the constants k and c are given by

$$k = K\sqrt{(A - B)^2 + 4ABC} \quad (17)$$

$$c = \frac{A + B + \sqrt{(A - B)^2 + 4ABC}}{A + B - \sqrt{(A - B)^2 + 4ABC}} \quad (18)$$

where A, B are the initial concentrations of water and ester, K is the velocity constant (natural logarithms) and C is the equilibrium constant. Naturally k and c have different values with reactions of other types. The quantity x in this case is the titer of the reacting solution, and may be observed in terms of alkali of unknown strength. Since there is acid present as catalyst $x_0 > 0$.

The experimental data[7] given by Harned and Pfanstiel for one run were plotted on a large scale, and four sets of values of x were read off the plot, with $\Delta t = 300$ minutes. These sets gave the values $A = 3.153, 3.144, 3.142, 3.110$. The trend observed here is possibly somewhat outside the experimental error, though it should be observed that the quantity $x_4 - x_3$ (≈ 13) is the difference of considerably larger quantities (≈ 60). At any rate, it is obvious that a satisfactory value of K could not be otained from these readings. The

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[5] This method of determination will be the subject of a future communication.

[6] Harned and Pfanstiel, THIS JOURNAL, 44, 2194 (1922).

[7] The quantity recorded by Harned and Pfanstiel is $x - x_0$, but since only differences in x appear in the calculations we may use $x - x_0$ in place of x.

mean value of A leads to $K = 2.20 \times 10^{-5}$, while Harned and Pfanstiel found $K = 2.342 \times 10^{-5}$. It is thus necessary to calculate K from the known value of c. The constants a, b involve x_0, x_∞ and therefore cannot be used.

Four sets of three readings each were interpolated with $\Delta t = 400$ minutes. From these sets, together with the value $c = -39.86$ calculated from the initial concentrations and equilibrium constant, the values $\alpha = 1.701, 1.700, 1.698, 1.691$ were calculated by successive approximations. The trend here, amounting to a total of 0.6%, may be partially due to inaccuracies introduced by the graphical interpolation. From the mean value of α one obtains $K = 2.365 \times 10^{-5}$, which is 1% higher than the value of Harned and Pfanstiel. This method of calculation eliminates the necessity of calculating the initial and final values of the titer as done by Harned and Pfanstiel. It should be emphasized that the value of α would be changed by less than 0.1% by a change of 5% in c.

Summary

An application of the methods of projective geometry to a series of measurements of a property x (of a system reacting in accord with the kinetic equation $kt = \ln c\,(a - x)/(b - x)$) which varies linearly with the progress of the reaction, taken at uniform time intervals, Δt, gives the result

$$A \equiv \frac{x_3 - x_2}{x_2 - x_1} \times \frac{x_4 - x_1}{x_4 - x_3} = 1 + 2 \cosh (k\,\Delta t)$$

By means of this result the necessity of obtaining initial and final values of x is eliminated.

The method is illustrated using the data of Harned and Pfanstiel on the hydrolysis of ethyl acetate.

NEW HAVEN, CONN. RECEIVED JANUARY 2, 1937

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Atomic Weights of Some Radiogenic Leads

BY G. P. BAXTER, J. H. FAULL, JR.,[1] AND F. D. TUEMMLER

In connection with the programs of the Committee on Geophysical Research of Harvard University and the Committee on Determination of Geologic Time of the National Research Council the atomic weights of some new specimens of radiogenic leads have been determined.

Samarskite from Glastonbury, Connecticut, U. S. A.—The original ground sample, weighing 1130 g., had been cleaned by gravity and magnetic methods by Mr. Harry Berman of the Harvard Mineralogical Laboratory. A preliminary analysis of a part of this material by R. C. Wells[2] shows 6.91% uranium, 3.05% thorium, 0.311% lead.

Treatment with redistilled hydrofluoric acid in platinum followed by repeated evaporation with nitric acid to remove the hydrofluoric acid and extraction of the insoluble residue with nitric acid, all in platinum, was carried out by Dr. C. M. Alter. The nitric acid solution on standing for several months deposited much columbic acid (40 g.). The dried insoluble residue weighed 970 g. This residue was found spectroscopically to contain most of the lead.

Lead was separated from the nitric acid solution by double precipitation of basic acetates and treating the filtrates with hydrogen sulfide. The original insoluble residue and that which separated from the nitric acid solution were digested for long periods with redistilled hydrochloric acid and the lead precipitated from the extract after neutralization with ammonium acetate. About 0.1 g. of lead was obtained from the extract, 1.6 g. from the insoluble residues, together representing about half the lead content of the original mineral.

Purification included the following processes: conversion of sulfide to sulfate through the chloride, solution of the sulfate in ammonium acetate and reprecipitation with hydrogen sulfide, solution of the sulfide in hydrochloric acid and conversion of the chloride to nitrate by repeated evaporation with nitric acid, four recrystallizations of the nitrate from nitric acid in quartz, conversion of nitrate to chloride with hydrochloric acid in quartz, four recrystallizations of chloride in quartz, and distillation of the chloride in dry hydrogen chloride in a quartz tube. All the product was used in one analysis. Lead was recovered from the solution of lead nitrate resulting from the first analysis and from the mother liquors remaining from the purification by precipitation as sulfide, and after conversion to the nitrate through the chloride it was re-purified as above.

Beaverlodge Lake Pitchblende.—This specimen was collected and contributed by Dr. Fred Joliffe from a quartz vein near Beaverlodge Lake, Northwest Territories, Canada, about one hundred miles south of Great Bear Lake. The mineral consists chiefly of an intimate mixture of pitchblende and specularite. Weighted averages from analyses of five lots of similar material, representing 3000

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[1] Research Associate in Geology in Harvard University, 1935. The present work is Paper No. 33 published under the auspices of the Committee on Geophysical Research and of the Division of Geological Sciences at Harvard University.

[2] R. C. Wells, Reports of the Committee on Determination of Geologic Time, of the National Research Council, April, 1935, and Sept., 1936.

lb. (1360 kg.), made in the Canadian Mines Branch, Ottawa, Canada, show 28.9% uranium and 1.57% lead with no thorium. Analysis by Baxter and Averill (see following paper) of material cleaned as below showed 51.2% uranium, 2.49% lead and no thorium.

After being crushed in a diamond mortar the pitchblende (514 g.) was finely pulverized in a specially cleaned grinder. Much of the iron ore was removed by suspension in water. The dried residue (433 g.) was then fractionated electromagnetically. This process was not particularly successful, apparently because of the intimate nature of the original mixture. A considerable quantity of material which could be picked up with an ordinary magnet, as well as a non-magnetic fraction, largely quartz, were thus eliminated. Galena could not be discovered in the non-magnetic fraction but a microscopic examination of a polished section by Dr. R. S. Moehlmann suggests a trace of this substance.

Of 415 g. remaining, 25 g. was set aside for analysis. The remaining 390 g. was treated with hot 8 *N* nitric acid and after separation from a slightly soluble residue of iron ore, the solution was evaporated with an excess of sulfuric acid and taken up with water. The residue (112 g.) was dissolved in hydrochloric acid and after separation from a nearly white residue (7 g.) the solution was evaporated with an excess of sulfuric acid and taken up with water. Very little lead sulfate was obtained from the hydrochloric acid solution of the iron ore.

The combined precipitates of lead sulfate were dissolved in ammonium acetate, and, after filtration of the solution, lead sulfide was precipitated. This was dissolved in hydrochloric acid, and the chloride was converted to nitrate by evaporation with nitric acid. At this point we had 14.6 g. of lead nitrate. This was further purified as described above in the case of the samarskite lead.

Katanga Pitchblende.—Some years ago Baxter and Alter[3] found the atomic weight of the lead contained in the yellow, hydrochloric acid soluble portion of a specimen of Katanga pitchblende to be 205.97 while that of lead from the black insoluble portion of the same specimen was found to be 206.00. A little later Hönigschmid, Sachtleben and Baudrexler[4] extracted a specimen of Katanga pitchblende with dilute hydrochloric acid and found the atomic weight of the lead in the extract to be 206.02. Recently Hecht and Kroupa [*Z. anorg. allgem. Chem.*, **226**, 248 (1936)] found the atomic weight of the lead contained in the black, less soluble portion of this specimen to be 206.04. Through the great kindness and generosity of Professor H. Buttgengach of the University of Liège we came into possession of a fine specimen of Katanga pitchblende weighing 1150 g. Aside from a considerable mass of yellow secondary minerals at one point, this specimen differed markedly from the one examined by Baxter and Alter in having a much larger proportion of veins of yellow secondary minerals. This was apparent even to the eye in the slightly greenish color, whereas the former specimen was black.

About 615 g. (free from masses of yellow) was broken up on a steel plate and ground in a steel mortar by hand. Nearly half, 298 g., was then extracted with 5% hydrochloric acid until lead chloride ceased to crystallize from the solution and the extract was nearly colorless. The black residue was then thoroughly washed and dried. The weight of this residue, 100 g., was 33% of the original whereas Baxter and Alter found 77% by a similar process with the earlier specimen.

The lead chloride which separated from the extract was collected. The remainder of the lead was precipitated as sulfate and converted to the chloride through the sulfide. In all 18.0 g. of lead chloride was obtained.

The black insoluble portion was dissolved in nitric acid and the greater part of the lead precipitated as chloride. The remainder was separated as sulfate and converted to chloride. The total weight of lead chloride was 8.73 g.

Both samples of lead chloride were converted to nitrate and purified as already described.

A rough determination of uranium was made in aliquot portions of both solutions from which the lead had been removed. The percentages of lead and uranium are given in the following table.

	Pb, %	U, %	Pb/U
Black	6.50	76.7	0.0847
Yellow	6.76	67.5	.1001
Whole	6.67	70.6	.0945

Baxter and Alter (*loc. cit.*) found the following percentages with the first specimen of Katanga pitchblende.

Black	6.7	74.9	0.089
Yellow	8.4	58.5	.144
Whole	7.1	71.2	.100

In an experiment to find the composition of the mineral more accurately, the proportion of black (pitchblende) decreased from 34.9% after one treatment with hydrochloric acid to 31.4 and to 30.8 after two additional treatments. Apparently the pitchblende dissolves slowly in 5% hydrochloric acid. Analysis of the hydrochloric acid extract and the residual material gave the following results:

	Pb, %	U, %	Pb/U
Black	6.48	77.2	0.0839
Yellow	6.74	68.5	.0983
Whole	6.66	71.2	.0935

These values are confirmed by the approximate analysis of the main bulk of material. The lead–uranium ratio in the case of the black material is in general agreement with values obtained by others.[5]

With all the radiogenic samples it was necessary to recover and repurify in order to secure the necessary material.

Common Lead.—Cerussite from Wallace, Idaho, U. S. A., was dissolved in nitric acid, and after filtration of the solution the lead nitrate was four times recrystallized in Pyrex vessels. The nitrate was then converted to chloride and the chloride four times recrystallized in quartz and twice redistilled in hydrogen chloride. Baxter and Grover[6] have already examined lead from this mineral and found it to possess a normal atomic weight (207.21).

The early stages in the purification of the various samples were carried on in Pyrex vessels, but in the crystallization

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[3] Baxter and Alter, THIS JOURNAL, **55**, 2785 (1933).

[4] Hönigschmid, Sachtleben and Baudrexler, *Z. anorg. allgem. Chem.*, **214**, 104 (1933).

[5] Bull. Nat. Research Council, "Physics of the Earth, IV, The Age of the Earth," 1931, pp. 367–369.

[6] Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

of the nitrate and chloride only quartz or platinum vessels were used. Residual silica and organic matter were eliminated easily in the final distillation of the chloride in hydrogen chloride in a quartz tube. No reagents were used which were not free from lead.

Spectroscopic examination of the final products in a carbon arc failed to show any evidence of impurity. Difficulty was experienced in securing graphite electrodes of sufficient purity, especially as regards silver, but this difficulty was finally overcome by the conventional method of heating the electrodes to 1000° in a current of chlorine in a quartz tube for long periods.

In every case the purified lead chloride was prepared for analysis by fusion in a current of dry hydrogen chloride containing more or less nitrogen. No variation in the composition of the salt with the proportion of hydrogen chloride could be detected. The salt was contained in a quartz boat placed in a quartz tube during the fusion. After the fusion it was transferred by means of a Richards bottling apparatus to the weighing bottle in which the empty boat had originally been weighed. The boat remained constant in weight throughout the whole series of experiments.

After the salt had been weighed it was dissolved in warm water to which a small amount of nitric acid had been added to prevent hydrolysis. The solution was then compared with silver in the conventional way, with the use of a nephelometer and 0.01 normal silver and chloride solutions, by the equal-opalescence method. In the precipitation, the solutions were 0.05 normal or less. The silver nitrate solution was always poured into the lead chloride solution.

The weights of lead chloride were corrected to vacuum by adding 0.000058 g. per gram and those of silver by subtracting 0.000031 g. per gram.

The Atomic Weight of Lead

Analyst	$PbCl_2$, g.	Ag, g.	Ag added, g.	Corrected wt. of Ag, g.	Ratio $PbCl_2$: 2Ag	At. wt. of Pb
			Common lead			
F	4.39335	3.40822	0.00000	3.40822	1.28905	207.211
F	3.49797	2.71380	− .00024	2.71356	1.28907	207.216
F	4.21579	3.27043	− .00010	3.27033	1.28910	207.222
T	4.27224	3.31422	+ .00005	3.31427	1.28904	207.210
T	5.99791	4.65309	− .00011	4.65298	1.28905	207.211
T	4.74688	3.68260	− .00010	3.68250	1.28904	207.209
T	3.99080	3.09571	+ .00010	3.09581	1.28910	207.222
				Average	1.28906	207.214
			Samarskite			
F	1.28803	1.00248	−0.00010	1.00238	1.28497	206.331
F	0.75523	0.58750	+ .00019	0.58769	1.28508	206.355
				Average	1.28503	206.343
			Beaverlodge Lake pitchblende			
F	2.61248	2.03519	−0.00030	2.03489	1.28384	206.088
F	2.75235	2.14453	− .00055	2.14398	1.28373	206.070
F	3.17452	2.47283	.00000	2.47283	1.28376	206.070
F	6.38415	4.97299	− .00052	4.97247	1.28392	206.099
F	4.01745	3.12924	− .00003	3.12921	1.28384	206.089
T	2.72167	2.12000	− .00010	2.11990	1.28387	206.093
T	2.17947	1.69745	+ .00020	1.69765	1.28382	206.082
				Average	1.28383	206.084
			Katanga pitchblende, hydrochloric acid extract			
F	3.43131	2.67331	−0.00025	2.67306	1.28366	206.049
F	3.52881	2.74926	− .00025	2.74901	1.28367	206.050
F	2.54121	1.97975	− .00015	1.97960	1.28370	206.057
T	4.28996	3.34186	+ .00020	3.34206	1.28363	206.041
T	4.84228	3.77222	− .00005	3.77217	1.28369	206.054
T	4.50429	3.50891	− .00002	3.50889	1.28368	206.053
				Average	1.283670	206.051
			Katanga pitchblende, unaltered			
F	1.70238	1.32609	+0.00015	1.32624	1.28361	206.038
F	1.60461	1.25088	− .00085	1.25003	1.28366	206.048
T	4.61797	3.59739	+ .00016	3.59755	1.28364	206.045
T	3.73794	2.91212	− .00006	2.91206	1.28361	206.037
				Average	1.28363	206.042

The average value for common lead is in good accord with recent evidence.

If the samarskite is free from common lead, the atomic weight to be expected from the proportions of uranium and thorium reported (see page 702) may be calculated on the assumptions (1) that uranium lead ($Pb^{206} + Pb^{207}$) has the atomic weight 206.00[7] and thorium lead (Pb^{208}) the value 207.96, and (2) that the relative rates of production of lead by uranium and thorium are 1.00: 0.36. The value thus found is 206.22, and indicates that about 12% of the lead in the samarskite is common lead and that in calculating the age of the samarskite the percentage of lead should be reduced by one-eighth. This assumes, however, that the relative proportions of uranium and thorium in the mineral have not altered with time.

The atomic weight of Beaverlodge Lake lead appears to be slightly higher than that of Great Bear Lake lead (206.06)[8] and since there is no appreciable amount of thorium in the pitchblende, about 7% of the lead is apparently common lead and the age 93% as high as calculated from the total percentage.

The Katanga pitchblende is noticeably different from that examined by Baxter and Alter.[3] In the first place the percentage of black unaltered material is one-half as large. In the second place not only does the lead have a higher atomic weight but the difference between the leads from the black and yellow material, if real, is in the opposite direction from that previously observed, 206.04 and 206.05 against 206.00 and 205.97. Furthermore, if thorium is absent in appreciable amount, as has generally been reported for Katanga lead, about 4% of the lead appears to be common lead and a corresponding correction is necessary in computing the age of the mineral from the percentages of lead and uranium.

Other determinations of the atomic weight of Katanga lead,[9] from both pitchblende and curite,

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[7] Baxter and Alter, This Journal, **57**, 470 (1935).

[8] Marble, *ibid.*, **56**, 854 (1934); Baxter and Alter, *ibid.*, **57**, 467 (1935).

[9] Hönigschmid and Birckenbach, *Ber.*, **56**, 1837 (1923), 206.048; Hönigschmid, Sachtleben and Baudrexler, *Z. anorg. allgem. Chem.*, **214**, 104 (1933), curite 206.031, yellow 206.023; Baxter and Alter,[8] curite 206.027.

have yielded values close to 206.03. The specimen described in this paper is particularly interesting in affording additional evidence that the atomic weight of Katanga lead is not constant and therefore by inference may contain common lead in varying proportions. This idea is substantiated by the recent work of Rose,[10] who finds the isotope Pb^{208} in a specimen of Katanga lead.

Summary

1. The atomic weights of certain radiogenic leads have been determined.

Source	Atomic weight
Cerussite, Wallace, Idaho, U. S. A. (common)	207.21
Samarskite, Glastonbury, Conn., U. S. A.	206.34
Pitchblende, Beaverlodge Lake, N. W. T., Canada	206.08
Pitchblende, Katanga, Africa	
Black, insoluble portion	206.04
Yellow, hydrochloric acid-soluble portion	206.05

2. It is pointed out that these values, together with the percentages of important components, point to the presence of several per cent. of common lead in all three radioactive minerals.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 9, 1937

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[10] Rose and Stranahan, *Phys. Rev.*, **50**, 792 (1936).

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Lead–Uranium Ratio of Beaverlodge Pitchblende

BY G. P. BAXTER AND M. E. AVERILL

A sample of the ground and mixed specimen of pitchblende from Beaverlodge Lake, N. W. T., Canada, which had been utilized in the determination of the atomic weight of lead described in the preceding paper, was analyzed for lead, uranium and thorium.

Weighed portions were first treated with 8 *N* nitric acid which dissolved the pitchblende but left most of the associated hematite insoluble. After separation, the hematite was dissolved in 7 *N* hydrochloric acid. Both solutions were evaporated to dryness, and siliceous residues were treated with hydrofluoric and sulfuric acids. Lead was separated from both solutions by evaporation with sulfuric acid, and the filtrate of the lead sulfate scavenged with hydrogen sulfide at suitable acidity. Lead so recovered was converted to sulfate and added to the main portions. All the lead sulfate was purified by solution in ammonium acetate and evaporation with sulfuric acid and the filtrate worked up for traces of lead.

Both the nitric and hydrochloric acid solutions were freed from iron by double precipitation of basic ferric acetate. Ammonium uranate was then precipitated from solution in an excess of ammonium carbonate, and collected. The filtrate was evaporated to dryness and after expulsion of ammonium salts a small amount of uranium was recovered as above.

The uranyl sulfate solution resulting from the extraction of lead from about 390 g. of mineral (see preceding paper) yielded several grams of rare earth oxalates, but we were unable to convince ourselves that thorium was present in more than traces. This is in accord with the results of analyses of similar material made by the Canadian Mines Branch (see preceding paper, p. 703).

TABLE I

Sample, g.	$PbSO_4$, g.	Pb, %	U_3O_8, g.	U, %	Pb/U
2.3005	0.0845	2.505	1.3963	51.47	0.0488
1.9146	.0699	2.490	1.1587	51.32	.0485
2.2185	.0807	2.481	1.3265	50.70	.0490
	Average	2.492		51.16	.0486

Baxter, Faull and Tuemmler (see preceding paper) have found the atomic weight of the lead contained in this sample of Beaverlodge pitchblende to be 206.08, indicating, in the almost complete absence of thorium, that about 7% of this lead is common lead. With the per cent. of uranium 51.16, and that of lead 2.318 (corrected for common lead) the Pb/U ratio is 0.0453. Analyses by the Canadian Mines Branch give 0.054 (see page 703 of preceding paper). Barring alteration and other unknown effects the approximate age of the mineral is 344 million years, while the logarithmic formula gives 336 million.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 9, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XVII. The Separation of Sol Rubber and Gel Rubber[1]

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

The sol rubbers, on which reliable physical and chemical measurements have been made, have been prepared either by fractional precipitation[2] from a mixture of benzene and alcohol, or by slow diffusion in absolute ethyl ether.

The separation of sol from gel rubber by diffusion assumes that the components can be separated from one another like sugar from sand and disregards the possibility that sol and gel rubbers may be mutually soluble in each other. If this latter condition actually exists, then the diffusion may only be expected to produce a two-phase, three-component system in equilibrium, and the relative amounts of sol and gel rubbers in the sol phase should be determined and not assumed. The same general reasoning applies to the fractional precipitation method of separation. Thus there is no "absolute" method of determining the relative quantities of sol and gel rubbers in any sample.

However, the relative efficiencies of separation by these two methods may be evaluated by preparing samples of "sol" rubber by each method and then attempting a further separation of each of these samples by the other method. This has been done with the following results.

Samples of sol rubber were prepared by fractional precipitation from sprayed latex rubber and were allowed to diffuse in ether. They dissolved rapidly and completely. They were quantitatively recovered unchanged from the ether by evaporation at reduced pressure. Also 30 g. of sprayed latex was allowed to diffuse in absolute ether, yielding 24 g. of soluble and 6 g. of insoluble material. The insoluble portion was leathery, rich in nitrogen; it was not analyzed further. The 24 g. of soluble material was recovered from the limpid ether solution by evaporation at reduced pressure, then subjected to fractional precipitation from a mixture of alcohol and benzene, with the following results:

Fractions	A_0	A_1	A_2	A_3	A_4	A_5	B
Amount, g.	3	6	1	1.5	1	0.5	10.5

One-half gram was lost during the operation. The A_0 fraction contained the so-called "acetone soluble" portion of natural rubber, since it was recovered by the evaporation of the benzene–alcohol mixture after completion of the fractionation. The A_1 fraction was found free of nitrogen, but not free of rubber degraded by oxidation, as it had a glossy appearance and gave 0.06% oxygen by the active hydrogen method[3] instead of 0.02 or 0.03% which is normal for good samples. This is not surprising, as it has always been found that two and sometimes three successive precipitations are needed to remove all traces of such oxidized material. Fractions A_2 to A_4 were typical high grade sol samples. Fraction A_5, which was very small and obtained with considerable difficulty, was obviously a mixture of A and B. Fraction B, the insoluble part, proved to be nitrogen free. In view of this last unexpected result, B was subjected to another fractionation, which removed only a small amount of impure A, amounting to about 2 g., and left a little more than 8 g. of a substance which was called BB. The characteristics of this BB fraction were: no nitrogen; 4.65% oxygen by combustion; 1.48% oxygen by active hydrogen measurement; slow solubility in benzene; extremely slow solubility in ether; no "leathery" feeling, no "tackiness" and no resemblance whatever to rubber degraded by oxidation. The high oxygen content of this material may safely be assumed to be due to an impurity.

The viscosities of the several fractions were measured in 0.23% solutions in benzene at 20°. The viscosities expressed in C. G. S. units × 10^3 were:

Benzene	A_1	A_2	A_3	A_4	BB
6.47	12.40	17.20	17.30	17.20	21.03

The low viscosity of A_1 is due to the accumulation therein of rubber degraded by oxidation. A_2 to A_4 are good samples of sol rubber. Their viscosities compare favorably with those recorded for thrice refractioned sol rubber (17.70) or twice re-

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[1] Original manuscript received October 22, 1936.

[2] THIS JOURNAL, 53, 2733 (1931).

[3] *Ibid.*, 57, 2318 (1935).

fractioned rubber (17.40 to 17.65) prepared in this Laboratory.

These results indicate quite clearly that a single diffusion of rubber into ether is insufficient completely to separate sol from gel rubber. They also show that while there is no absolute criterion by which the fractional precipitation method may be judged, it is decidedly more efficient than the ether diffusion method.

Summary

Sol rubber prepared by a single diffusion in ether can be separated into two components by fractional precipitation, whereas sol rubber prepared by a single fractional precipitation completely diffuses in ether, thus indicating the superiority of the fractional precipitation method as a means of preparing sol rubber.

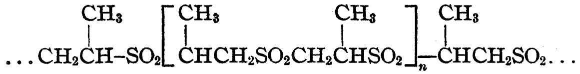
COLUMBUS, OHIO RECEIVED FEBRUARY 23, 1937

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

The Reaction between Sulfur Dioxide and Olefins. V.[1] The Structure of the Polysulfones from Olefins of the Type RCH=CH$_2$

BY F. J. GLAVIS, L. L. RYDEN AND C. S. MARVEL

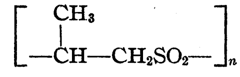
It has been demonstrated[2] that propylene and sulfur dioxide combine to form a polysulfone (I)



$$\ldots \mathrm{CH_2\overset{\overset{CH_3}{|}}{C}H{-}SO_2}\left[\mathrm{\overset{\overset{CH_3}{|}}{C}HCH_2SO_2CH_2\overset{\overset{CH_3}{|}}{C}HSO_2}\right]_n\mathrm{\overset{\overset{CH_3}{|}}{C}HCH_2SO_2}\ldots$$

I

in which the propylene units are oriented so that like parts of the hydrocarbon residues are linked through the sulfone groups. The hydrolysis of the polysulfone with alkali gave products which could not be reconciled with the structure II,

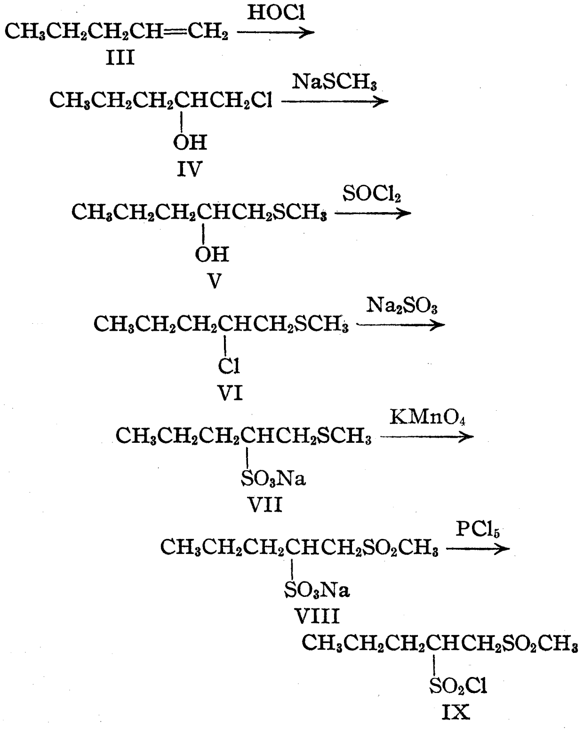


$$\left[\mathrm{{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_2SO_2{-}}\right]_n$$

II

which had previously been assigned to the addition product.[3] The experiments described in this communication were undertaken to determine whether the polysulfones from other olefins of the type RCH=CH$_2$ would be structurally comparable to propylenepolysulfone (I), or would have a simple symmetrical unit similar to that indicated in formula II.

1-Pentenepolysulfone, prepared as described previously,[4] can be hydrolyzed by warming it with 20% sodium hydroxide solution to yield *n*-butyraldehyde and a sodium salt of composition $C_6H_{13}S_2O_4Na$. This salt can be oxidized readily by hydrogen peroxide to give a compound $C_6H_{13}S_2O_5Na$, which, with phosphorus pentachloride, yields a sulfonyl chloride melting at 64–65°. The same sulfonyl chloride (IX) has been synthesized from 1-pentene by the following series of reactions



$$\mathrm{CH_3CH_2CH_2CH{=}CH_2} \xrightarrow{\mathrm{HOCl}}$$

III

$$\mathrm{CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_2Cl} \xrightarrow{\mathrm{NaSCH_3}}$$

IV

$$\mathrm{CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_2SCH_3} \xrightarrow{\mathrm{SOCl_2}}$$

V

$$\mathrm{CH_3CH_2CH_2\underset{\underset{Cl}{|}}{C}HCH_2SCH_3} \xrightarrow{\mathrm{Na_2SO_3}}$$

VI

$$\mathrm{CH_3CH_2CH_2\underset{\underset{SO_3Na}{|}}{C}HCH_2SCH_3} \xrightarrow{\mathrm{KMnO_4}}$$

VII

$$\mathrm{CH_3CH_2CH_2\underset{\underset{SO_3Na}{|}}{C}HCH_2SO_2CH_3} \xrightarrow{\mathrm{PCl_5}}$$

VIII

$$\mathrm{CH_3CH_2CH_2\underset{\underset{SO_2Cl}{|}}{C}HCH_2SO_2CH_3}$$

IX

This synthesis of the sulfonyl chloride (IX) establishes the structure of the sulfonic acid salt $C_6H_{13}S_2O_5Na$ (VIII). Likewise, it shows that the salt $C_6H_{13}S_2O_4Na$ must have the structure shown in formula XII. 1-Pentenepolysulfone must, accordingly, have the structure shown in formula X, and thus be strictly comparable to propylenepolysulfone (I) in the arrangement of the hydrocarbon residues.

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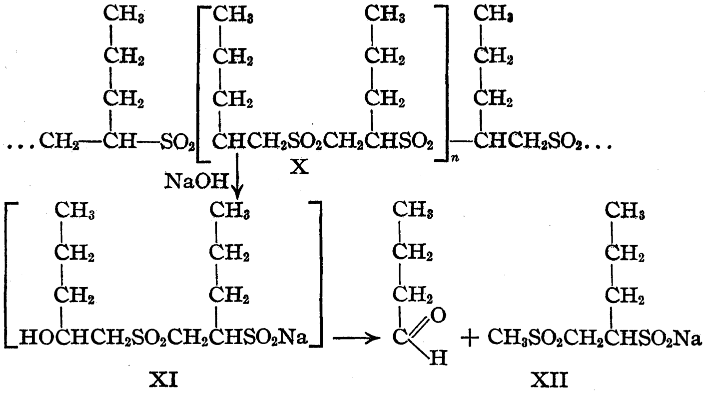
[1] For the fourth paper in this series, see Ryden and Marvel, THIS JOURNAL, **58**, 2047 (1936).

[2] Hunt and Marvel, *ibid.*, **57**, 1691 (1935).

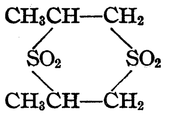
[3] Staudinger and Ritzenthaler, *Ber.*, **68**, 458 (1935).

[4] Ryden and Marvel, THIS JOURNAL, **57**, 2311 (1935).



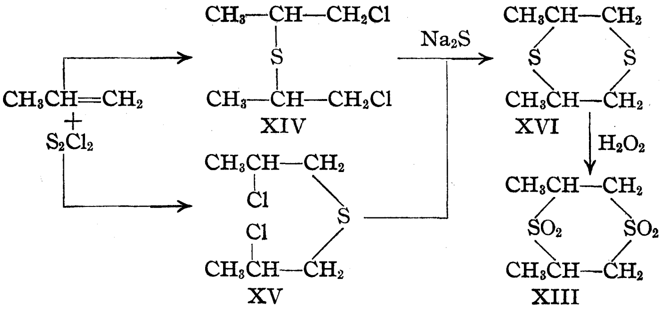
X XI XII

A further proof that these two polysulfones have similar structural units has been obtained by studying the breakdown of the polymers in liquid ammonia solutions. Propylenepolysulfone dissolves in liquid ammonia, and on evaporation of the solvent and crystallization of the residue from an organic solvent, yields the same cyclic disulfone (XIII) which was previously obtained[2,3] by the



XIII

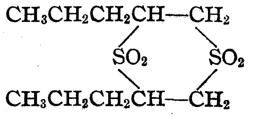
action of cold alkalies on propylenepolysulfone. This cyclic disulfone (XIII), whose structure was established[2] by alkaline cleavage, has now been synthesized in the following manner



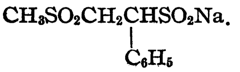
XIV XV XVI XIII

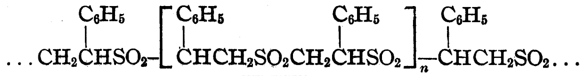
The structure of the intermediate dichlorosulfide is probably that given in formula XV[5] rather than that given in formula XIV, but the same cyclic disulfide (XVI) would be obtained from either.

1-Pentenepolysulfone in liquid ammonia is also broken down into a cyclic disulfone (XVII), and the same product was obtained from 1-pentene by the synthesis used above in the case of propylene.

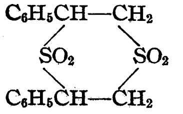


XVII

Styrenepolysulfone (XVIII), which has not been described previously, has now been prepared by the general method which has been developed for other polysulfones,[4] and its structure has been established by hydrolysis with alkali to give benzaldehyde and a salt of a sulfone sulfinic acid,  $CH_3SO_2CH_2\underset{C_6H_5}{\underset{|}{C}}HSO_2Na$. In liquid ammonia solution, styrenepolysulfone is converted to a cyclic disulfone (XIX), and the structure of this product was established by its synthesis from styrene by the methods described above for the analogous products from propylene and 1-pentene.



XVIII

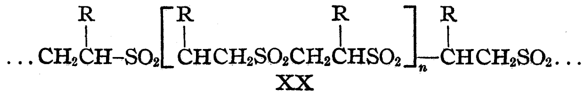


XIX

1-Octenepolysulfone and 1-nonenepolysulfone[4] also undergo rearrangement in liquid ammonia solution to yield dimeric products which are presumably cyclic disulfones of the general structure which has been established in the above cases.

There can no longer be doubt that, in the addition of sulfur dioxide to an olefin of the type $RCH{=}CH_2$, there is a definite orientation of the hydrocarbon residues, so that like parts are joined through sulfone linkages (XX).

The fact that these olefin–sulfur dioxide addition polymerization reactions so generally yield the "head to head–tail to tail" type of polymer seems to us to make it logical to assume that other addition polymerization reactions may take place in a similar manner, and thus to make it desirable to investigate more carefully the structure of the products of such reactions.



XX

Experimental

Styrenepolysulfone.—A mixture of 10 cc. of styrene, 10 cc. of liquid sulfur dioxide, 2 cc. of ethyl alcohol, 2 drops of

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(5) Pope and Smith, *J. Chem. Soc.*, **119**, 396 (1921).

30% hydrogen peroxide and 5 cc. of paraldehyde containing peroxides was placed in a pressure bottle and allowed to stand for twelve to eighteen hours at room temperature. The paraldehyde must be added at the start of the reaction in this preparation as otherwise only polystyrene is formed. The reaction mixture was poured into 100 cc. of ether, and the polymer was collected on a filter. When the reaction mixture was poured into water, it was very difficult to obtain a good product free from water. The yield of polysulfone was 0.5 to 2.5 g. in various experiments. The product darkens on heating and melts, with decomposition, at 185–190°. It is slightly soluble in acetone, but insoluble in most other common organic solvents.

Anal. Calcd. for $(C_8H_8SO_2)_n$: S, 19.05. Found: S, 18.64.

1-Octenepolysulfone.—A mixture of 10 cc. of 1-octene, 10 cc. of liquid sulfur dioxide, 2 cc. of ethyl alcohol, 2 cc. of 3% hydrogen peroxide and 5 cc. of "old" paraldehyde was allowed to stand as described above. The product was precipitated by pouring the reaction mixture into water. The yield was 2 to 4 g. in various runs. This product is first rather pliable, but eventually sets to a very hard product. It is soluble in acetone, but not in other common organic solvents. It becomes opaque at 100°, and melts, with decomposition, at 175–200°.

Anal. Calcd. for $(C_8H_{16}SO_2)_n$: S, 18.18. Found: S, 17.82.

Alkaline Hydrolysis of 1-Pentenepolysulfone.—A suspension of 2 g. of 1-pentenepolysulfone in 10 cc. of 20% sodium hydroxide was heated to boiling, and a current of steam was passed through the mixture. The distillate was condensed and collected in a vessel containing a solution of 1 g. of 2,4-dinitrophenylhydrazine, 75 cc. of alcohol, 10 cc. of concentrated sulfuric acid and water to give a total volume of 250 cc. A precipitate of *n*-butyraldehyde 2,4-dinitrophenylhydrazone came down. The yield was 1.2 g. (85%) of a product melting at 121.5–122°. The literature[6] gives the melting point of *n*-butyraldehyde 2,4-dinitrophenylhydrazone at 122°.

The alkaline residue, after steam distillation had removed all of the butyraldehyde, was evaporated to dryness, and this residue was extracted with hot 95% alcohol. On cooling this solution, a white crystalline salt separated. The yield of salt was about 1 g. (60%). The salt contained one molecule of water of crystallization when dried in a desiccator over phosphorus pentoxide at room temperature, but lost this at 125°. The analyses for carbon, hydrogen and sodium were made on the anhydrous sample.

Anal. Calcd. for $C_6H_{13}S_2O_4Na \cdot H_2O$: H_2O, 7.1. Found: H_2O, 7.0. *Anal.* Calcd. for $C_6H_{13}S_2O_4Na$: C, 30.9; H, 5.5; Na, 9.7. Found: C, 30.4; H, 5.3; Na, 10.1.

Oxidation of the Salt $C_6H_{13}S_2O_4Na$.—To a solution of 10 g. of the above salt in 20 cc. of water was added 30 cc. of 30% hydrogen peroxide solution over a period of about thirty minutes. Considerable heat was liberated during the oxidation. The reaction mixture was allowed to stand for about fifteen minutes, and then evaporated to dryness on a steam-bath. The residue was recrystallized from 200 cc. of hot 95% alcohol. The yield was 7 g. (69%) of a white crystalline salt. The product was dried at 100° at 3 to 4 mm. before analyzing.

Anal. Calcd. for $C_6H_{13}S_2O_5Na$: S, 25.4. Found: S, 25.2.

Preparation of the Sulfonyl Chloride.—The salt obtained in the preceding experiment was recrystallized four times from alcohol and dried. Then 1 g. of this highly purified salt was ground in a mortar with 1 g. of phosphorus pentachloride. One hundred cubic centimeters of ice water was added immediately, and an oily precipitate separated. On stirring the mixture, the oil solidified. The solid was separated and recrystallized from a mixture of petroleum ether and benzene. It melted at 64–65°.

Anal. Calcd. for $C_6H_{13}S_2O_4Cl$: S, 27.12. Found: S, 26.99.

1-Chloro-2-pentanol.—1-Pentene was converted to the chlorohydrin, according to the method which Coleman and Johnstone used for 1-chloro-2-cyclohexanol.[7] From 50 g. of 1-pentene, there was obtained 37 g. (43%) of 1-chloro-2-pentanol, b. p. 68–75° at 30 mm.; d^{20}_{20} 1.037; n^{20}_D 1.4520.

Anal. Calcd. for $C_5H_{11}OCl$: Cl, 26.35. Found: Cl, 26.78.

1-Methylthiol-2-pentanol.—The directions for the preparation of methylthiolethyl alcohol[8] were used for this synthesis. From 35 g. of the above chlorohydrin, there was obtained 18 g. (45%) of a product boiling at 90° under 18 mm.; d^{20}_{20} 0.943; n^{20}_D 1.4792.

Anal. Calcd. for $C_6H_{14}SO$: S, 23.88. Found: S, 22.78.

1-Methylthiol-2-chloropentane.—The directions for the preparation of β-chloroethylmethylsulfide[9] were adopted for this synthesis. From 18 g. of the above methylthiol alcohol and 21 g. of thionyl chloride, there was obtained 14 g. (70%) of a product boiling at 84–86° at 20 mm.; d^{20}_{20} 1.0090; n^{20}_D 1.4860.

Anal. Calcd. for $C_6H_{13}SCl$: Cl, 23.26. Found: Cl, 23.48.

Sodium 1-Methylthiol-2-pentanesulfonate.—To a solution of 14 g. of sodium sulfite in 50 cc. of water, 12.5 g. of 1-methylthiol-2-chloropentane was added over a period of about one hour. The mixture was well stirred with a mechanical stirrer, and heating and stirring were maintained for an hour after the addition of the chloro compound. The solution was evaporated over a water-bath, and the residue was recrystallized from 95% alcohol. The yield of salt was about 2 g.

Anal. Calcd. for $C_6H_{13}S_2O_3Na$: S, 10.44. Found: S, 10.68.

1-Methylsulfonepentane-2-sulfonyl Chloride.—To a solution of 3 g. of the above salt in 10 cc. of water was added 1 drop of 10% sodium hydroxide solution, and enough 5% potassium permanganate solution so that the color persisted after the solution was boiled. The excess potassium permanganate was then destroyed with hydrogen peroxide solution, and the reaction mixture was filtered. The filtrate was evaporated to dryness, and the residue was re-

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(6) Brady and Elsmine, *Analyst*, **51**, 77 (1926); Allen, THIS JOURNAL, **52**, 2955 (1930).

(7) Coleman and Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 151.

(8) Windus and Shildneck, "Organic Syntheses," Vol. XIV, John Wiley and Sons, Inc., New York, 1934, p. 54.

(9) Kirner and Windus, *ibid.*, p. 18.

Table I

Cyclic Disulfones from Polysulfones

Polysulfone from	Yield of cyclic disulfone, %	Solvent for crystallization	M. p., °C.	Molecular formula	Analyses, % Calcd. C	H	S	Found C	H	S
Propylene	35	Mixture of dioxane and water	334	[a]						
1-Pentene	40	Alcohol	257	$C_{10}H_{20}S_2O_4$	44.8	7.46	23.8	44.8	7.03	23.5
1-Octene	40	Dioxane and acetic acid	265	$C_{16}H_{32}S_2O_4$	..	..	18.18	..	...	18.02
1-Nonene	14	Alcohol or benzene	260–261	$C_{18}H_{36}S_2O_4$	56.9	9.48	...	57.4	10.02	...
Styrene	25	Alcohol, dioxane and glacial acetic acid	280	$C_{16}H_{16}S_2O_4$	..	..	19.05	..	...	19.35

[a] This product is identical with a product isolated by treatment of propylenepolysulfone with cold sodium hydroxide solution, and reported as melting at 320°.[2]

crystallized from alcohol four times. The yield of recrystallized salt was 1.3 g. (40%). This salt was then converted to the sulfonyl chloride in the manner described for the sulfone–sulfonate salt obtained from the breakdown of 1-pentenepolysulfone.

The sulfonyl chloride from this synthetic salt melted at 64–64.5°, and when a sample of this synthetic product was mixed with the sulfonyl chloride prepared from the breakdown of the polysulfone, the mixture melted at 64–65°.

Alkaline Hydrolysis of Styrenepolysulfone.—A mixture of 10 g. of styrenepolysulfone and 100 cc. of 10% sodium hydroxide solution was distilled with steam. The distillate contained benzaldehyde, which was identified by preparing the 2,4-dinitrophenylhydrazone, which melted at 235°, and showed no depression in melting point when mixed with an authentic specimen of the benzaldehyde derivative.[10] The solution remaining in the distilling flask was filtered and evaporated to dryness. The resulting salt was recrystallized from alcohol. The yield was 4 g. Ten grams of this salt was oxidized by dissolving it in 20 cc. of water and treating with 30 cc. of 30% hydrogen peroxide solution. This reaction mixture was evaporated, and the sulfonic acid salt was recrystallized from alcohol.

Anal. Calcd. for $C_9H_{11}S_2O_5Na$: S, 22.38. Found: S, 22.51.

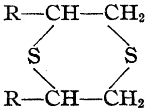
Liquid Ammonia Cleavage of Polysulfones.—Several polysulfones were treated with liquid ammonia to test their solubility. It was observed that those which dissolved were changed by the treatment. The long polymeric molecules were broken up and cyclic disulfones were produced. The experiments were carried out by dissolving about 1 g. of polysulfone in 50–100 cc. of liquid ammonia, and then allowing the solvent to evaporate. The crystalline residue was then recrystallized from an organic solvent. The results are summarized in Table I.

Neither cyclohexenepolysulfone nor isobutylenepolysulfone would dissolve in liquid ammonia, and were recovered unchanged after the treatment. 2-Pentenepolysulfone dissolved slowly in liquid ammonia, and the polymer was destroyed, but no crystalline products could be isolated.

2,6-Disubstituted-1,4-dithians.—Three representatives of this series of compounds were prepared from the olefins by first adding sulfur monochloride according to the procedure of Pope and Smith,[5] and then converting the crude β,β'-dichlorosulfides to the 1,4-dithians by the action of sodium sulfide. In each case, to 72 g. (0.5 mol) of sulfur monochloride was added 1 mol of olefin. After the completion of the addition reaction, the crude mixture was added to a solution of 0.5 mol of sodium sulfide in absolute alcohol, prepared as described by Bost and Conn.[11] The reaction mixture was boiled overnight, and then poured into 2 liters of 25% sodium chloride solution. The dithian derivative was extracted with petroleum ether (b. p. 40–110°), and purified by distillation under reduced pressure. The results of these experiments are given in Table II.

Table II

2,6-Disubstituted-1,4-dithians

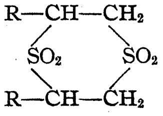


R=	Yield, %	B. p., °C.	Press., mm.	$n^{20}D$	Sp. gr. 20/20	Analyses, % Calcd. S	Found S
CH_3—	14	85– 87	12	1.5420	1.080	43.2	42.5
							42.2
n-C_3H_7—	9	145–155	20	1.5255	1.002	31.37	31.5
C_6H_5—	11	190–195	30	1.6060	1.143	23.53	23.15

2,6 - Disubstituted - 1,4 - dithian - 1,4 - bis - (dioxides).—These synthetic cyclic disulfones were obtained by oxidizing about 2 g. of the corresponding 1,4-dithian derivative in 10 cc. of glacial acetic acid with 5 cc. of 30% hydrogen peroxide. The reaction mixture was heated to boiling under a reflux condenser for about fifteen minutes, and diluted with about 50 cc. of water. The precipitate which came down was then recrystallized from dioxane or alcohol. The synthetic product in each case proved to be identical with the product obtained by dissolving the corresponding polysulfone in liquid ammonia. These experiments are recorded in Table III.

Table III

Comparison of Synthetic Cyclic Disulfones with those Obtained from Polymeric Sulfones



R=	Yield from dithian, %	M. p. of synthetic product, °C.	M. p. of product from polymer, °C.	Mixed m. p., °C.
CH_3—	90	332	334	334
n-C_3H_7—	90	254–256	257	257
C_6H_5—	80–85	279	280	279

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(10) Curtius and Dedichen, *J. prakt. Chem.*, **50**, 265 (1894).

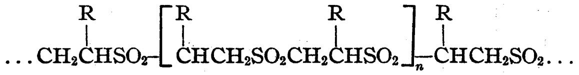
(11) Bost and Conn, "Organic Syntheses," Vol. XV, John Wiley and Sons, Inc., New York, 1935, p. 72.

Summary

1. Those polysulfones prepared from sulfur dioxide and olefins, which dissolve in liquid ammonia, are converted by this treatment into cyclic disulfones.

2. Styrene (phenylethylene) adds sulfur dioxide to give a polysulfone.

3. Evidence is presented to show that polysulfones prepared from olefins of the type $RCH=CH_2$ have the general formula



$$\ldots CH_2\overset{R}{C}HSO_2-\left[\overset{R}{C}HCH_2SO_2CH_2\overset{R}{C}HSO_2\right]_n-\overset{R}{C}HCH_2SO_2\ldots$$

in which like parts of the hydrocarbon residues are joined to each other by sulfone linkages.

URBANA, ILLINOIS RECEIVED JANUARY 29, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in the Ketone Sugar Series. VI. The Effect of Zinc Chloride on Ketose Acetates

BY FRANCIS B. CRAMER[1] AND EUGENE PACSU

In preparing new sugar derivatives for testing the isorotation rules in the aldose group, Hudson and co-workers have made extensive use of zinc chloride dissolved in acetic anhydride as a reagent in converting the β-acetates into the α-forms. An earlier physico-chemical investigation of the process by Jungius[2] showed that in the case of glucose pentaacetates equilibrium was reached when the proportion was nine moles of the α- to one mole of the β-form. In the case of most aldose acetates the equilibrium contains the two forms in similar proportion. Exceptions are found in the pentaacetates of galactofuranose[3] and galactoseptanose[4] where the equilibrium is in favor of the β-isomers. In 1915, Hudson and Brauns[5] attempted to apply this method to β-pentaacetylfructose. When zinc chloride was added to a solution of this substance in acetic anhydride, only a very small change in rotation was observed whereas a large one was anticipated. Since some coloration occurred, the authors evidently ascribed the change in rotation to slight decomposition and after recovering about one-third of the starting material and conducting confirmatory experiments, concluded that the method was not applicable in the ketose series. It has now been discovered that the small change in rotation observed by Hudson and Brauns was due to the formation of the new isomer described in Part V[6] as the true α-pentaacetylfructopyranose.

The structure of β-pentaacetylfructose is generally accepted as that of a normal acetate possessing a <2, 6> ring. The evidence leading to this conclusion is extensive and will not be reviewed here. To establish the structure of the new fructose acetate as the normal α-pentaacetate, it would be sufficient to show that it differs from the known β-compound only in the configuration of carbon atom 2. If this glycosidic carbon atom were selectively inverted, the β-pentaacetate should result.

When a trace of zinc chloride was added to the acetic anhydride solution of the new fructose acetate, the rotation dropped rapidly, changing sign, and within a few minutes became constant at −107°. From the rotations of α- and β-pentaacetylfructose in acetic anhydride (42.3 and −122°, respectively) it may be calculated that the equilibrium mixture contained 91% of the β-form. When the solution was worked up a large amount of β-pentaacetylfructose was obtained.

Similarly, when pure β-pentaacetylfructose was treated with zinc chloride in acetic anhydride after the manner of Hudson and Brauns,[5] the rotation again became −107°. On carefully working up this mixture, a small amount of the α-compound was isolated in pure form.

This interconversion of the two acetates gives definite proof that the new compound is the true α-pentaacetylfructose <2,6>. Supporting evidence is afforded by the method of preparation, both α- and β-pentaacetates being formed simultaneously by replacing the chlorine atom in β-acetochlorofructose with the acetoxyl radical. In

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[1] This paper is based upon a thesis submitted by Francis B. Cramer to the Faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Jungius, *Z. physik. Chem.*, **52**, 101 (1905).

[3] Hudson and Johnson, THIS JOURNAL, **37**, 1519 (1915).

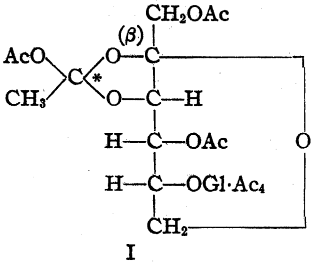
[4] Micheel and Suckfüll, *Ann.*, **502**, 85 (1933).

[5] Hudson and Brauns, THIS JOURNAL, **37**, 2736 (1915).

[6] Pacsu and Cramer, *ibid.*, **57**, 1944 (1935).

addition, both isomers are reconverted into the starting material by treatment with titanium tetrachloride in chloroform solution. The structure of the new pentaacetate is thus established.

The discovery of the effect of zinc chloride in acetic anhydride solution upon the acetates of fructose suggested the application of this isomerization to the acetates of other ketoses. In Part I,[7] there have been described four isomeric octaacetates of turanose which are referred to by giving the ordinal number of their sequence in discovery. The third octaacetate has been shown in Part III[8] to have an open-chain structure. Since this compound can possess no α- or β-isomer, it holds no interest in connection with the action of zinc chloride. The first and fourth octaacetates have been described as representing a pair of isomeric orthoester acetates which differ only in the configuration of the newly formed asymmetric carbon atom C* (I). This carbon atom is not part of the turanose skeleton and both compounds have been regarded as derivatives of β-turanose. The second octaacetate (II) has been *assumed* to be an α-derivative of turanose with a normal <2, 6> ring in the fructose residue.



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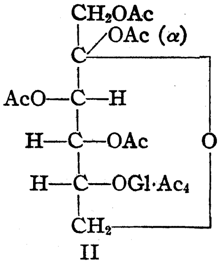

II

When the solution of the second octaacetate in acetic anhydride was treated with zinc chloride at room temperature, a rapid though small change in rotation from the original value of 106.5° to the equilibrium value of 98° was observed. Although this equilibrium can scarcely be regarded as favorable, an attempt was made to prepare the expected new acetate by this method. Out of 10 g. of the second octaacetate 7 g. of pure starting material was recovered. The residual sirup could not be brought to crystallization. The rotation of this material was 63.1° in acetic anhydride, indicating a considerable concentration of the expected β-compound. Treatment of the sirup on the steam-bath with acetic anhydride and sodium acetate produced no change in the rotation of the material. However, when the sirup dissolved in acetic anhydride was treated with zinc chloride at room temperature, the rotation rose almost immediately to the equilibrium value of 98°. Upon working up the solution and recrystallizing the product, the pure second octaacetate was obtained in good yield.

The above evidence indicates definitely that a fifth octaacetate of turanose of β-configuration exists. The position of the equilibrium with zinc chloride as well as several other facts[7] sharply differentiate the behavior of the turanose acetate under consideration from that of the normal α-pentaacetylfructose. The structure of the second octaacetate of turanose may, therefore, be regarded as still open to investigation.

Attention may now be turned to the first and fourth octaacetates of turanose (I) which have been characterized in Part I[7] as a diastereomeric pair having orthoester structure. The first has the low positive rotation of 20.5°. The other has a positive rotation of 103.2°. When this higher-rotating isomer was treated with zinc chloride in acetic anhydride solution, the rotation dropped rapidly to 40° indicating the formation of an equilibrium mixture containing 87% of the first octaacetate which was isolated easily from the reaction mixture. This bears a striking resemblance to the behavior of the normal pentaacetates of fructose under like conditions, where the positive-rotating α-compound is converted 90% into the negative-rotating β-compound. Indeed, comparison of these two pairs of ketose acetates reveals much similarity and little difference.

The lower-rotating acetates may be converted[7,9] into the corresponding β-acetohalogeno compounds, and the latter react with a metal acetate to give the higher-rotating acetates.[6,7] These higher-rotating acetates when treated according to standard methods give the original β-acetohalogeno compounds as sole products.

Further facts for comparison now appeared highly desirable. The problem is more difficult because no test for orthoester structure in the case of sugar acetates is available. The conversion of these acetates to glycosides where orthoester structure can be proved may involve unpredictable changes in structure.[10]

Attention was directed to the acetohalogeno compounds as the only derivatives which are

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(7) Pacsu, THIS JOURNAL, **54**, 3649 (1932).

(8) Pacsu and Rich, *ibid.*, **55**, 3018 (1933).

(9) Brauns, *ibid.*, **42**, 1846 (1920).

(10) Pacsu, *ibid.*, **55**, 2451 (1933).

prepared directly from the acetates. It is known that acetobromoturanose reacts with methyl alcohol and silver carbonate to give an orthoester glycoside acetate.[10] When similarly treated, acetobromofructose also yielded an orthoester glycoside acetate. Some of Schlubach's normal α-tetraacetylmethylfructoside was simultaneously formed, exactly as when acetochlorofructose was used.[11]

It has been reported in Part I[7] that acetobromoturanose undergoes a marked change when dissolved in pyridine. The observed rotation, at first negative (−3.1°), becomes strongly positive (6.3°) where it remains constant. When a stronger solution is prepared, it soon turns to a jelly, the latter shortly becoming a clear solution again. The aged solution acquires the ability to reduce an acetone solution of potassium permanganate very rapidly. This reaction was assumed to be due to the formation of a ketene-acetal which would have definitely indicated orthoester structure for the acetobromoturanose. It has now been found that this behavior is closely paralleled by a solution of acetobromofructose in pyridine. A large drop of the highly negative rotation almost to zero was observed and the solution acquired the ability to reduce an acetone solution of potassium permanganate with great rapidity.

Acetochlorofructose has been shown to undergo no change when dissolved in pyridine.[11] The same behavior was displayed by acetochloroturanose. Attempts to prepare the pyridinium salts of the acetochloro compounds by the method of Fischer[12] resulted in the recovery of unchanged starting material.

A correct interpretation of the experimental results enumerated above is not an easy matter. The use of Hudson's rules provide two apparent facts to start with. These facts are, first, α- and β-pentaacetylfructose do not possess orthoester structure and, second, the first and fourth octaacetates of turanose do not possess the same structures as the fructose acetates.

The first conclusion follows from the fact that the value for $b_{\text{fruct. Ac.}}$ can be used to calculate the rotations of the methyl- and ethylfructoside acetates. These latter compounds are of normal structure and have properties sharply differentiating them from the known methyl- and ethylfructoside acetates of orthoester structure.[11]

The second conclusion follows from the fact that it is impossible by means of the customary mathematical manipulation of the rotations of turanose octaacetates to obtain a value for a_{OAc} which would agree satisfactorily with the value of a_{OAc} calculated from the α,β pair of fructose pentaacetates <2, 6>. It may, therefore, be concluded that the glycosidic portion of the turanose acetate molecule possesses a fundamentally different structure from that of the glycosidic portion of the fructose acetates.

At present, only two types of structure about the glycosidic carbon atom of the acetylated sugars are recognized, these being the normal and the orthoester structures. Unfortunately, as stated above, it is not possible to determine by any chemical or physical means whether a sugar acetate possesses an orthoester structure or a normal structure. The only conclusion, therefore, is that the acetates of fructose possess normal structures and the first and fourth acetates of turanose have orthoester structures. Careful consideration of the behavior of the acetohalogeno compounds derived from these acetates reveals little or nothing concerning the structures of the parent acetates. On the basis of Hudson's rules, the similarity between the pairs of turanose octaacetates and fructose pentaacetates which has been mentioned earlier must be regarded as coincidental until new contradictory evidence is discovered.

Experimental Part

Action of Zinc Chloride on the Pentaacetates of Fructose.—The specific rotation[13] of α-pentaacetylfructose in pure acetic anhydride was found to be 42.3°. In 20 cc. of distilled acetic anhydride was dissolved 0.3132 g. of this substance and the solution was made up to 25 cc. with a solution of 0.1 g. of fused zinc chloride in 20 cc. of the same solvent. The following specific rotations were observed after 54, 85, and 270 seconds, respectively: 12, −10.4, and −71.5°. After twenty minutes the rotation remained constant at −107°. Two and eight-tenths grams of pure α-pentaacetylfructose was treated similarly and the equilibrated solution was evaporated to a sirup *in vacuo*, the residue taken up in chloroform, and washed with sodium bicarbonate solution until neutral. The chloroform solution was then dried with calcium chloride, filtered, and evaporated to a thin sirup *in vacuo*. This was taken up in absolute ether and placed in the ice box. After separation as described in Part V[6] and recrystallization, 1.9 g. of β-pentaacetylfructose and 0.028 g. of the original α-pentaacetate were isolated in pure form.

Ten grams of pure β-pentaacetylfructose was dissolved by heating in 10 cc. of distilled acetic anhydride. To the

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(11) Pacsu, THIS JOURNAL, **57**, 745 (1935).

(12) Fischer, *Ber.*, **43**, 1750 (1910).

(13) Unless otherwise indicated, the rotations here recorded were measured at 20°, using light of the wave length of the sodium D lines, and chloroform as solvent.

cooled solution was added 0.1 g. of fused zinc chloride dissolved in 5 cc. of the same solvent. After standing for half an hour at room temperature, the solution was poured into cracked ice and triturated with ice water until the gummy residue solidified. This was filtered off, washed and dried. Seven grams of material having the specific rotation −113° was obtained. The acidic aqueous mother liquor and washings were combined, neutralized with sodium bicarbonate, and placed in the ice box, when 1.9 g. of material having the specific rotation −97.3° separated. The aqueous mother liquor of this was extracted three times with chloroform, the extracts combined, dried with calcium chloride and evaporated *in vacuo*. The residual sirup was taken up in absolute ether and placed in the ice box. The solution deposited 0.7 g. of sticky crystals which had the rotation −96.6°. Upon working up the three crystalline fractions as before, 7.2 g. of pure starting material was recovered, and 0.2 g. of α-pentaacetylfructose was isolated in pure form.

Action of Zinc Chloride on the Second Octaacetate of Turanose.—The specific rotation of the second octaacetate of turanose in acetic anhydride was found to be 106.5°. A 0.2656-g. sample of this material was dissolved in 20 cc. of distilled acetic anhydride. The solution was made up to 25 cc. using a solution of 0.1 g. of fused zinc chloride in 20 cc. of the same solvent. Four minutes after mixing the specific rotation had fallen to 101°. In thirty minutes the rotation became 98° and remained constant at that value. Ten grams of the pure second octaacetate was now dissolved in 50 cc. of distilled acetic anhydride by warming on the steam-bath. To the cooled solution was added 0.1 g. of fused zinc chloride dissolved in 10 cc. of the same solvent. In thirty minutes the rotation of the solution became constant. After an additional half hour, the mixture was poured into 400 g. of crushed ice. After three hours of intermittent stirring, the material was left overnight in the ice box, the suspension of white powder was filtered and washed with water. The dried solid was taken up in 25 cc. of absolute ether and placed in the ice box where it crystallized; yield 7.4 g., and specific rotation, 101.8°. After two recrystallizations from hot alcohol, 7 g. of pure starting material was recovered. On systematically working up the mother liquors including the acidic aqueous mother liquor, 2.9 g. of a sirup was obtained having a specific rotation of 67.4°. In an acetyl estimation by the method of Kunz[14] 0.280 g. of material used 31.9 cc. of 0.1 normal sodium hydroxide solution. The value calculated for 8 acetyl groups is 33.0 cc. A sample of this material weighing 0.5776 g. was dissolved in 10 cc. of distilled acetic anhydride. The specific rotation in this solvent was 63.1°. To this solution was added 0.05 g. of fused zinc chloride and the rotation rose within ten minutes to 94.2° where it remained constant. The solution was poured into 100 g. of crushed ice. After two hours the solid material was filtered out, washed with ice water, and dried; yield 0.4 g. After two recrystallizations from hot alcohol, 0.3 g. of beautiful crystals of the α-octaacetate having the specific rotation 105.5° was obtained. Another portion of the sirup was acetylated with fused sodium acetate and acetic anhydride by heating the mixture on the steam-bath for half an hour. Upon working up the mixture a sirupy product was obtained showing the unchanged rotation of 67.6°.

Action of Zinc Chloride on the Fourth Octaacetate of Turanose.—In 8 cc. of distilled acetic anhydride was dissolved 0.1012 g. of the fourth octaacetate of turanose and the solution made up to 10 cc. with a solution of 0.1 g. of fused zinc chloride in 20 cc. of the same solvent. The following specific rotations were observed after 1.5, 5, 10, and 30 minutes, respectively: 84.5, 60.8, 47.3 and 41.5°. After two hours, the rotation remained constant at 40.6°. The mixture was then worked up in the usual way using sodium bicarbonate solution and the product recrystallized from absolute ether; yield, 0.06 g. having the specific rotation 28.1°. After recrystallizing from alcohol, 0.048 g. of the first octaacetate of turanose having the correct specific rotation 19.6° was obtained.

Action of Pyridine on β-Acetochloro-fructose and -turanose.—Following the procedure of Fischer in preparing the pyridinium salt of acetobromoglucose,[12] 5 g. of crystalline acetochlorofructose was dissolved in 10 cc. of pyridine freshly distilled from barium oxide. The solution was kept for two days in a glass-stoppered flask. The only observable change was a slight darkening. Neither the aged nor the fresh solution reduced an acetone solution of potassium permanganate. The solution was poured into a beaker and kept in a vacuum desiccator over concentrated sulfuric acid until the odor of pyridine had almost disappeared. The sticky brown residue was extracted with *ca.* 50 cc. of absolute ether at room temperature. A small gummy residue remained. The ether solution at 0° deposited 3.2 g. of the pure starting material. The same experiment was repeated with 0.38 g. of acetochloroturanose dissolved in 25 cc. of absolute pyridine. The yield of recovered unchanged starting material was 0.25 g. of crystals showing the correct m. p. of 166°.

Action of Pyridine on β-Acetobromofructose.—In 25 cc. of absolute pyridine was dissolved 1.0822 g. of crystalline acetobromofructose. Three and one-half minutes after adding the solvent the specific rotation was −188°. In ten minutes the rotation had dropped to −166° and in one hour to −50°. After three hours the rotation reached the value of −5.53°. The direction of the change then reversed and the rotation slowly became more negative. After slowly changing for three weeks, the rotation became constant at −45°. In 10 cc. of absolute pyridine was dissolved 2.0 g. of acetobromofructose. In a few minutes a gelatinous precipitate formed in the clear solution and on shaking soon redissolved. The material slowly acquired the ability to reduce an acetone solution of potassium permanganate. After several days, the reduction took place within a few seconds. No pyridinium hydrobromide separated on careful addition of absolute ether in contrast to the behavior of acetobromoturanose as reported in Part I.[7]

Reaction of β-Acetobromofructose with Methyl Alcohol.—The general procedure given in Part IV[11] for the acetochloro compound was followed. To a suspension of 10 g. of silver carbonate in 25 cc. of absolute methyl alcohol in a glass-stoppered flask was added 2.3 g. of acetobromofructose, and the mixture vigorously shaken. A very rapid reaction ensued, the evolution of carbon dioxide ceasing in less than one minute. After shaking for fifteen

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(14) Kunz and Hudson, This Journal, **48**, 1892 (1926).

minutes, the solution no longer gave a test for labile bromine when boiled with alcoholic silver nitrate and nitric acid. The solution, which showed no action toward Fehling's solution, consisted of a mixture of α-methylfructoside tetraacetate and a large amount of β-methylfructoside tetraacetate with orthoester structure. In order to prove the presence of the latter compound, a few drops of the solution was diluted with 2 cc. of cold water and 1 drop of dilute hydrochloric acid was added. After *ca.* ten seconds at room temperature, considerable reduction took place on boiling with Fehling's solution. To isolate the normal α-methylfructoside tetraacetate, the reaction mixture was now filtered free of silver salts, and evaporated *in vacuo* to a thick sirup. To this was added 50 cc. of boiling water, and the mixture kept at 100° with vigorous shaking to hydrolyze the orthoester. In ten minutes a clear yellow solution was obtained. After filtering with charcoal, the colorless solution was placed in the ice box. Upon seeding with α-methylfructoside tetraacetate, the solution deposited 0.28 g. of crystals having the specific rotation 42.3°, and m. p. 110–111°. The aqueous mother liquor reduced Fehling's solution strongly due to the tetraacetylfructose formed by the hydrolysis of the orthoester. The crystalline material obtained above reduced Fehling's solution only after long boiling with acid.

Summary

The recent discovery of the true α-pentaacetylfructose $<2, 6>$ has made possible for the first time the study of the behavior of the α,β pair of ketose acetates toward different agents.

It has been shown that the use of zinc chloride as a catalyst in the isomerization of the sugar acetates is applicable in the ketose series.

The application of this method to the first and fourth octaacetates of turanose of supposed orthoester structure has revealed a strong similarity in properties to those of the normal fructose acetates. This similarity has been shown to exist also between the corresponding acetohalogeno derivatives of fructose and turanose although the former are generally assigned normal structure whereas an orthoester structure had been advanced for the latter. Application of Hudson's rules confirms the normal structure of the fructose acetates but excludes such for the turanose acetates.

The formation of a fifth octaacetate of turanose from the so-called second or α-octaacetylturanose $<2, 6>$ has been observed. Marked difference in the behavior of this pair from that of the normal fructose pentaacetates makes the structure assumed for the second octaacetate of turanose uncertain.

The behavior of the crystalline acetochloro compounds of fructose and turanose toward pyridine has been found to be radically different from that of the corresponding acetobromo compounds.

PRINCETON, N. J. RECEIVED FEBRUARY 13, 1937

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

The Synthesis of Long Chain Substituted Isocyclics and Similarly Substituted Adipic Acids.[1] The Preparation of γ-*t*-Octylcyclohexanol, Hexene, Hexanone, Hydroxylamine, Amine, Phenol and β-*t*-Octyl Adipic Acid

BY JOSEPH B. NIEDERL AND RICHARD A. SMITH

Introduction

On account of the renewed interest and present-day commercial importance of the alkyladipic acids[2] it was considered appropriate to give in this communication an account of the synthesis of a long chain adipic acid, namely, the β-diisobutyladipic acid. For the preparation of this acid (VI) the γ-diisobutylcyclohexanol (I), obtained by the catalytic hydrogenation of *p*-diisobutylphenol (*p*-($\alpha,\alpha,\gamma,\gamma$-tetramethyl)-butylphenol),[3] served as the starting material in the subsequent oxidation processes. The cyclic ketone (γ-diisobutylcyclohexanone) (III) as well as the above β-diisobutyladipic acid (VI) were obtained in excellent yields employing the conventional oxidation processes.[4] The oxime (IIIa) of the above ketone was prepared in the usual manner and from this oxime the γ-diisobutylcyclohexylhydroxylamine (IV) was prepared by catalytic hydrogenation. More strenuous reduction with sodium and alcohol yielded the γ-diisobutylcyclohexylamine (V). Dehydration of the γ-diisobutylcyclohexanol (I) yielded the corresponding γ-

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[1] Presented at the St. Petersburg meeting of the American Chemical Society, March 27, 1934. Original manuscript received July 25, 1934.

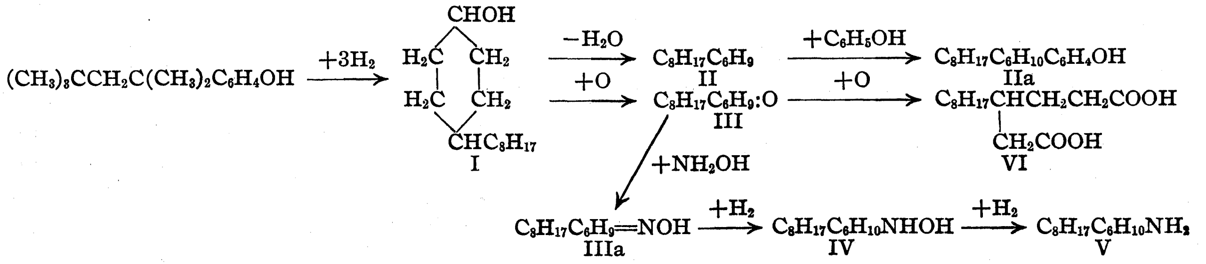
[2] R. Kuhn, *Ber.*, **67**, 1130 (1934); K. Ruzicka, *Helv. Chim. Acta*, **9**, 249 (1926); **16**, 1323, 1339 (1933); Ziegler and co-workers, *Ann.*, **504**, 94 (1933); R. P. Perkins, U. S. Patent 1,960,211 (1934).

[3] J. B. Niederl, U. S. Patent 2,008,032 (1935); Niederl and co-workers, THIS JOURNAL, **55**, 257 (1933).

[4] A. Baeyer, *Ann.*, **278**, 100 (1894); Bouveault and Locquin, *Bull. soc. chim.*, [4] **3**, 438 (1908); Mannich, *Ber.*, **39**, 1595 (1906); Wislicenus and Mager, *Ann.*, **275**, 363 (1893); Ciamician and Silber, *Ber.*, **46**, 3077 (1913).

diisobutylcyclohexene (II) which in turn was condensed with phenol according to the method of Niederl and co-workers[5] to form a *p*-diisobutylcyclohexylphenol (IIa).

The methods of preparation and the structural relationship of the various new products described herein may be illustrated as follows



as the reaction proceeded. At the completion of the reaction (one-half hour after heat ceased to be evolved), the whole was allowed to cool. The product was separated and purified by vacuum distillation. The yield was approximately 85%; b. p. 142–144° (11 mm.); sp. gr. (20°) 0.9850; $n^{23}\text{D}$ 1.4768.

Anal. Calcd. for $C_{14}H_{26}O$: C, 80.0; H, 12.6. Found: C, 79.3; H, 12.3.

Experimental

Methods of Preparation

I. 4-(α,α,γ,γ-Tetramethyl)-butylcyclohexanol-1.—This compound was prepared by catalytic hydrogenation under high pressure and at elevated temperature of *p*-diisobutylphenol:[6] m. p. 55.5–56°; b. p. 148–150° (11.5 mm.).

Anal. Calcd. for $C_{14}H_{18}O$: C, 79.24; H, 13.21. Found: C, 79.16; H, 13.22.

II. 4-(α,α,γ,γ-Tetramethyl)-butylcyclohexene-1.—To 42 g. of the above *t*-octylcyclohexanol (I) 0.6 cc. of sulfuric acid (95%) was added and the mixture, contained in a Claisen flask, was heated on an oil-bath at 130–140° at 12 mm. The *t*-octylcyclohexene distilled over as rapidly as it formed: b. p. 113° (12 mm.), sp. gr. (25°) 0.8565; $n^{25}\text{D}$ 1.4741.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.60; H, 13.40. Found: C, 86.76; H, 13.37.

IIa. 4-(α,α,γ,γ-Tetramethyl)-butyl-1-(4-hydroxy)-phenylcyclohexane.—To a 0.1 molar mixture of the above *t*-octylcyclohexene (II) and phenol, 2 cc. of sulfuric acid (95%) was added slowly at 60° and the mixture was then allowed to stand overnight. The reaction product was worked up according to the procedure of McGreal and Niederl[7] and then subjected to fractional distillation under reduced pressure: m. p. 81° (uncorr.); b. p. 110–120° (2 mm.).

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.28; H, 11.10. Found: C, 83.52; H, 11.08.

III. 4-(α,α,γ,γ-Tetramethyl)-butylcyclohexanone-1.—Twenty-eight grams of the above *t*-octylcyclohexanol (I) was added in four portions over a period of half an hour to a solution of 30 g. of crystalline potassium dichromate, 150 cc. of water, and 25 g. of sulfuric acid (sp. gr. 1.84) contained in a flask fitted with a mechanical stirrer. The temperature was held at 50–55° by means of an external bath. Heat was evolved during the additions, and a double compound which formed during the reaction disappeared

IIIa. 4-(α,α,γ,γ-Tetramethyl)-butylcyclohexanone-1-oxime was prepared from the above cyclic ketone (III) in an alcoholic solution of hydroxylamine with heating on a steam-bath. The oxime was recrystallized from 70% alcohol; m. p. 152° (uncorr.).

Anal. Calcd. for $C_{14}H_{27}NO$: C, 74.66; H, 12.00; N, 6.23. Found: C, 74.60; H, 12.21; N, 6.17.

IIIb. Sodium Bisulfite Addition Compound of 4-(α,α,γ,γ-Tetramethyl)-butylcyclohexanone-1.—A saturated solution of sodium bisulfite (50% excess) was shaken with the *t*-octylcyclohexanone (III); white crystals separated. The crystals were heated with boiling 50% alcohol and cooled. A mass of fine snow-white crystals separated which were filtered off and washed with water and alcohol. A saturated solution of sodium carbonate was used to regenerate the ketone in a pure form.

IV. 4-(α,α,γ,γ-Tetramethyl)-butylcyclohexylhydroxylamine-1.—Ten and one-half grams octylcyclohexanonoxime (IIIa), 1 g. of active nickel catalyst, and 150 cc. of 95% ethyl alcohol as a solvent were shaken up in an atmosphere of hydrogen at a pressure of 50 pounds per sq. in. (3.3 atm.). One molar equivalent of hydrogen was taken up. The liquid was decanted, acidified with hydrochloric acid, and evaporated to dryness on a steam-bath. The resulting crystalline compound was purified by dissolving in the minimum quantity of absolute alcohol and precipitating with absolute ether; m. p. 240–245° with decomposition.

Anal. Calcd. for $C_{14}H_{30}ONCl$: N, 5.32. Found: N, 5.29.

V. 4-(α,α,γ,γ-Tetramethyl)-butylcyclohexylamine-1.—Two and one-half grams of octylcyclohexanonoxime (IIIa) was dissolved in 100 cc. of absolute alcohol, and the whole brought to boiling. Three grams of sodium in small pieces was added rapidly. The whole was then acidified with hydrochloric acid, cooled, and the solid sodium chloride filtered off. The solid was washed with dilute hydrochloric acid; the hydrochloric acid solutions were combined and evaporated to dryness. The residue was treated with 40% sodium hydroxide and extracted twice with ether. Concentrated hydrochloric acid was added to the ether extracts and the whole was again evaporated to dryness

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(5) Niederl and co-workers, THIS JOURNAL, **56**, 2412 (1934); **55**, 3025, 4151, 4549 (1933).

(6) Röhm and Haas Company, Philadelphia, Penna., private communication.

(7) McGreal and Niederl, THIS JOURNAL, **57**, 2625 (1935).

on a steam-bath. The product was purified by recrystallizations from alcohol and acetone, m. p. 260–265° with decomposition.

Anal. Calcd. for $C_{14}H_{30}NCl$: N, 5.67. Found: N, 5.79.

VI. β - (α,α,γ,γ - Tetramethyl) - butyl - adipic Acid.—This compound was prepared both by the oxidation of the corresponding alcohol (I), cyclohexene (II) and ketone. Oxidations with and without the aid of a vanadium catalyst were employed. The most satisfactory oxidation was the following: 125 cc. of nitric acid (50%) was heated to 110° in a flask fitted with a stirrer. A pinch of sodium vanadate (about 0.2 g.) was added. A few grams of the *t*-octylcyclohexanol (I) was then added, fumes of oxides of nitrogen being given off immediately. The whole was then cooled to 60° by means of an external bath. Then more diisobutylcyclohexanol (I) was added (42 g.) at such a rate that the temperature was kept within 55–65°. Rapid stirring was maintained throughout the entire reaction; the stirring was continued for one hour after the final addition of alcohol. Upon completion, the whole was cooled with an external ice-bath, and the mass of white crystals filtered off and air dried. The product was quite pure at this stage. The crystals were further purified by recrystallization from concentrated nitric acid; a saturated solution was made up at 65°, and allowed to cool. The yield of pure product was 60%; m. p. 133–134° (uncorr.).

Anal. Calcd. for $C_{14}H_{26}O$: C, 65.11; H, 10.08. Found: C, 64.94; H, 9.88.

This work was done in collaboration with the Chemical Laboratories of the Röhm and Haas Company, Philadelphia, Penna., who furnished the intermediate hydrogenated *p*-diisobutylphenol.

Summary

1. γ-Diisobutylcyclohexanol, hexene, hexanone, oxime, hydroxylamine amine and phenol were prepared, identified and their physical and chemical characteristics described.

2. β-Diisobutyladipic acid was prepared by a simple oxidation process, indicating the feasibility of preparing long chain adipic acid by similar methods.

NEW YORK, N. Y. RECEIVED JANUARY 14, 1936

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

The Synthesis of Long Chain Substituted Isocyclics and Similarly Substituted Adipic Acids.[1] The Preparation of α-*t*-Octylcyclohexanone and a Method of Indirect Structure Proof for Ortho and Para Alkylphenols

BY JOSEPH B. NIEDERL AND J. BRADLEY WHITMAN

Introduction

The existing methods of structure proof for ortho and para substituted alkylphenols can be divided into two main classes, the direct[2] and the indirect[3] methods. Both types of methods can be subdivided into analytical methods, and into procedures involving synthesis. The following report gives an indirect method which appears to be capable of wide application and which has served as a method of structure proof for ortho- and para-substituted alkylphenols. First a comparison of the solid derivatives (esters) of the hydrogenation products of the phenols, α- or γ-cyclohexanols may be made. These cyclohexanols can then be further oxidized conveniently to the corresponding α- or γ-cyclohexanones, of which solid, crystalline derivatives, such as the oximes, the semicarbazones, the phenylhydrazones, etc., can be prepared easily and again subjected to comparison by mixed melting points. Since the α-alkylcyclohexanones can be prepared independently by the interaction of the sodium salt of the desmotropic cyclohexanol,[4] ortho substitution of the original phenol certainly can be proved conclusively by the absence of a depression in the melting points of the cyclo ketone derivative, other constants having been determined to be identical. On further oxidation of the alkylcyclohexanones, only the γ-alkylcyclohexanone yields the corresponding β-alkyladipic acid, whereas the α-alkylhexanone yields adipic acid itself as the final oxidation product. Schematically such a structure proof can be presented as follows

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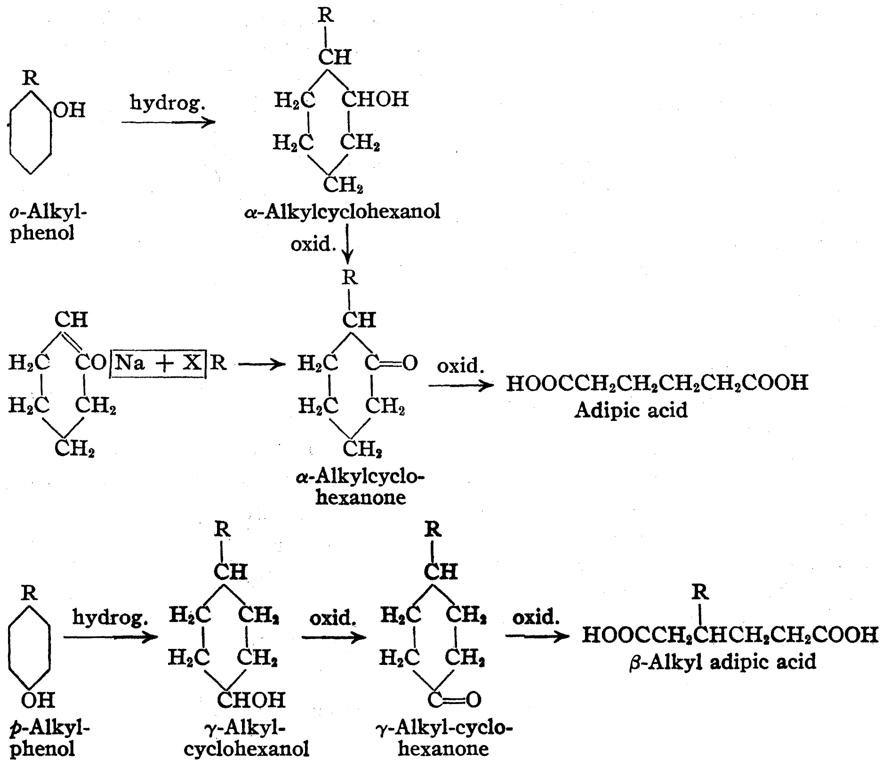
(1) Original manuscript received July 25, 1934.

(2) Barth, *Ann.*, **154**, 360 (1870); Jacobsen, *Ber.*, **11**, 376, 570, 1058, 2052 (1878); Friedländer and Low, German Patent 170,230 (1906); Oppenheim and Pfaff, *Ber.*, **8**, 887 (1875); Königs and Heymann, *ibid.*, **19**, 1704 (1886).

(3) Koerner, *Gazz. chim. ital.*, 419 (1874); Noelting, *Ber.*, **18**, 2687 (1885); Meyer and Jacobsen, "Lehrbuch der org. Chemie," Vol. II, Part 1, Veit and Co., Leipzig., 1902, p. 68.

(4) Haller, *Compt. rend.*, **138**, 1140 (1904); Tarbouriech, *ibid.*, **149**, 604 (1909); Bouveault and Chereau, *ibid.*, **142**, 1086 (1906); Mannich and co-workers, *Ber.*, **39**, 1594 (1906); **41**, 467 (1908); Koetz and co-workers, *J. prakt. Chem.*, [2] **80**, 505 (1909); *Ann.* **350**, 210 (1906).



Application of this method of structure proof was made in the following case and manner. The oxime of the γ-diisobutylcyclohexanone prepared from the catalytic hydrogenation product of *p*-diisobutylphenol by subsequent mild oxidation of the hexanol to the corresponding γ-diisobutylhexanone, was proved to be different by the depression in the melting point, from the oxime of the α-diisobutylcyclohexanone prepared from the desmotropic sodium enolate of cyclohexanone and diisobutylene hydrogen bromide, $(CH_3)_3CCH_2C(CH_3)_2Br$.[5] Oxidation of the γ-diisobutylcyclohexanone yielded β-diisobutyl adipic acid, whereas oxidation, under similar conditions, of the α-isomer, gave adipic acid itself as the main and final oxidation product.

Experimental

2 - (α,α,γ,γ - Tetramethyl) - butylcyclohexanone - 1.—One molar equivalent of sodamide was added slowly to 100 g. of cyclohexanone in 300 cc. of absolute ether. When no more ammonia was evolved (after about four or five hours), one mole of diisobutylene hydrobromide, prepared by the addition of hydrogen bromide to diisobutylene,[6] was added and the whole refluxed for two days. The product was washed with water, dried over sodium sulfate, the ether distilled off and vacuum distilled. Large amounts of diisobutylene were recovered; yield 16%; b. p. 140–144° (11 mm.).

2 - (α,α,γ,γ - Tetramethyl) - butylcyclohexanonoxime - 1 was prepared from the above ketone and hydroxylamine; m. p. 147–148° (uncorr.); mixed melting point with the oxime prepared from the 4-isomer 123–125°.

Anal. Calcd. for $C_{14}H_{27}NO$: C, 74.66; H, 12.00; N, 6.23. Found: C, 74.33; H, 11.70; N, 6.50.

The Oxidation of 2-(α,α,γ,γ-Tetramethyl)-butylcyclohexanonoxime.—The oxime was oxidized with 50% nitric acid in the presence of a vanadium catalyst in exactly the same manner as was the 4-diisobutylcyclohexanol in the concomitant communication by J. B. Niederl and R. A. Smith. The reaction did not proceed as smoothly. The product melted at 152°. The analysis indicated it to be adipic acid. A mixed melting point with pure adipic acid, obtained commercially, was the same as either sample alone.

Summary

1. α-Diisobutylcyclohexanone was prepared from cyclohexanone by the method of Haller, involving the action of the diisobutylene hydrohalide upon the desmotropic sodium cyclohexenolate.

2. An indirect method of structure proof for ortho- and para-substituted alkylphenols was described.

NEW YORK, N. Y.

RECEIVED JANUARY 14, 1936

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[5] Butlerow, *Ann.*, **189**, 47 (1877).

[6] P. W. Hodges, M.Sc. Thesis, New York University, 1935.

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

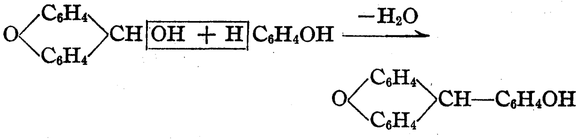
Monohydroxyphenylxanthanes[1]

BY JOSEPH B. NIEDERL AND WILLIAM F. HART[2]

In the course of the systematic investigation of the condensation of alcohols with phenols[3,4] the reaction of xanthydrol with phenols was studied using glacial acetic acid, sulfuric acid or anhydrous aluminum chloride as condensing agent. The phenolic products obtained in each case were the corresponding hydroxyphenylxanthanes. The method employing glacial acetic acid was found to be most satisfactory, indicating the extreme reactivity of the hydroxyl group in xanthydrol. This fact had been noticed previously also by Fabre, Fosse and Robyn,[5] who condensed the three dihydroxybenzenes (resorcinol, catechol and hydroquinone) and their derivatives with xanthydrol and obtained the respective mono and dixanthyl compounds.

This reaction was extended to include phenol (I), *p*-chlorophenol (II), *p*-hydroxyacetophenone (III), α-naphthol (IV), *p*-*t*-(2′-phenyl)-butylphenol (V), and *p*-*t*-(2′-phenyl)-amylphenol (VI). Condensation was effected in each case and crystalline products were obtained also in cases where conventional methods for obtaining crystalline derivatives had failed. Such phenols were the *p*-*t*-(2′-phenyl)-butylphenol and *p*-*t*-(2′-phenyl)-amylphenol.[6] These compounds were first condensed with xanthydrol and then methylated to yield the crystalline 1-methoxy-2-xanthyl-4-(2′-phenyl)-butylbenzene (V) and 1-methoxy-2-xanthyl-4-(3′-methyl-2′-phenyl)-butylbenzene (VI), respectively.

The reaction in all these condensations appears to involve the elimination of one mole of water between the hydroxyl group of xanthydrol with either the ortho or para hydrogen atom of the respective phenol, as follows



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH\boxed{OH + H}C_6H_4OH \xrightarrow{-H_2O} O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH—C_6H_4OH$$

The products obtained by condensing phenol itself with xanthydrol (I), as well as its methyl ether (Ia), were found to be identical with 4-hydroxyphenylxanthane and 4-methoxyphenylxanthane, respectively, prepared by Gomberg and co-workers.[7]

Of interest is the observation that compounds in the xanthyl group (xanthydrol, xanthone, etc.) in general, and also the relatively non-toxic xanthylphenols described above, the phenol coefficient of which is less than one,[8] appear to produce in adult ovariectomized rats and mice physiological symptoms which are usually associated with feeble estrogenic substances.

Experimental

Condensation Method.—Four grams (0.02 mole) of xanthydrol was dissolved in 6 cc. of glacial acetic acid and the mixture warmed gently on the water-bath to effect solution. To this solution was added 2 g. (0.04 mole) of phenol, whereupon the solution turned red. The condensation flask was stoppered and allowed to stand for twenty-four hours at room temperature. Excess of water was then added to wash out acetic acid and unreacted phenol. If the phenol employed was not water soluble the condensation product was washed further with ammonium hydroxide of sufficient concentration (usually 10%) to dissolve that particular phenol. The condensation product was then dissolved in benzene and this solution was extracted three times with Claisen solution (50% potassium hydroxide plus an equal volume of methanol). The Claisen solution insoluble fraction contained unreacted xanthydrol, xanthone and other products not yet identified. The combined Claisen solution extracts were washed with benzene, diluted with water and acidified with dilute hydrochloric acid (10%). This acid solution was extracted with ethyl acetate or ether, the solvent removed and the residue recrystallized from an appropriate solvent, such as methanol or benzene. Decolorizing carbon was used to remove highly colored impurities. When the phenolic product obtained was difficult to crystallize, its methyl ether was prepared by methylation with dimethyl sulfate.

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[1] Presented at the New York meeting of the American Chemical Society, April, 1935. (Original manuscript received April 4, 1936.)

[2] Abstracted from Part II of the thesis presented by William F. Hart to the Faculty of the Graduate School of New York University in partial fulfilment for the degree of Doctor of Philosophy, April 1, 1936.

[3] Niederl and co-workers, THIS JOURNAL, **53**, 3390 (1931); **55**, 284, 4549 (1933); **57**, 2625 (1935).

[4] J. B. Niederl, U. S. patent 2,029,539 (1936).

[5] R. Fabre, *Ann. chim.*, [9] **18**, 49 (1922); Fosse and Robyn, *Compt. rend.*, **145**, 813 (1908); **160**, 1538 (1923).

[6] McGreal and Niederl, THIS JOURNAL, **57**, 2625 (1935); Zimmerman, M.Sc. Thesis, New York University, 1936; B. Gutchin, M.Sc. Thesis.

[7] Gomberg and co-workers, THIS JOURNAL, **34**, 1529 (1912); **47**, 198 (1925).

[8] The authors wish to thank Dr. Wm. A. Feirer of Sharp and Dohme, Inc., Philadelphia, for determining the phenol coefficients of these compounds.

	Compound	Formula	M. p., °C.	Analyses, % Calcd. C		Found C	
				C	H	C	H
I	4-Hydroxyphenylxanthane	$C_{19}H_{14}O_2$	150	83.19	5.15	83.63	5.80
	(a) Methyl ether	$C_{20}H_{16}O_2$	112–113	83.28	5.56	83.15	5.64
	(b) Benzoate	$C_{26}H_{18}O_3$	183–184	82.51	4.79	82.17	4.32
II	5-Chloro-2-hydroxyphenylxanthane	$C_{19}H_{13}O_2Cl$	132	73.89	4.24	74.38	4.42
III	2-Hydroxy-5-acetylphenylxanthane	$C_{21}H_{16}O_3$	189	79.71	5.09	79.77	5.03
IV	α-Hydroxy-*x*-xanthylnaphthalene	$C_{23}H_{16}O_2$	195	85.15	4.97	84.91	5.10
V	1-Methoxy-2-xanthyl-4-(2′-phenyl)-butylbenzene	$C_{30}H_{28}O_2$	210	85.66	6.71	85.19	6.95
VI	1-Methoxy-2-xanthyl-4-(3′-methyl-2′-phenyl)-butylbenzene	$C_{31}H_{30}O_2$	202	85.71	6.91	85.95	7.05

The same phenolic condensation products were obtained when using sulfuric acid as the condensing agent. In this case 0.02 mole of sulfuric acid was added to 0.02 mole of xanthydrol and 0.04 mole of phenol. The initial condensation was carried out at 0° and was worked up as described above. Anhydrous aluminum chloride was also employed as a condensing agent; in this instance benzene was used as inert solvent and the reaction mixture was refluxed for eight hours.

Summary

A number of new monohydroxyphenylxanthanes were prepared by simple condensation methods. The physical, chemical and some physiological properties of these crystalline condensation products have been described.

NEW YORK, N. Y. RECEIVED FEBRUARY 23, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

"Hydro-polymerization"[1]

BY V. N. IPATIEFF[2] AND V. I. KOMAREWSKY[2]

In our study of catalytic hydrogenation, it was of great importance to investigate whether olefinic hydrocarbons could be hydrogenated by hydrogen *in statu nascendi*, obtained by decomposing water with iron in the presence of different salts as promoters.[3] For this purpose amylene and isobutene were heated (300°) in a rotating autoclave in the presence of water, reduced iron and magnesium chloride. The results were negative, although a sufficient amount of hydrogen was formed under this condition. In order to see whether magnesium chloride may act as a poison for amylene hydrogenation, a usual hydrogenation of amylene was made with hydrogen, using iron as catalyst in the presence of magnesium chloride. The hydrogenation took place,[4] but an additional new phenomenon was observed, namely, simultaneous polymerization and hydrogenation which produced *decane*. Therefore, investigation was made of other polymerization agents, such as aluminum chloride, zinc chloride and phosphoric acid,[5] in combination with different hydrogenating catalysts (Fe·NiO). In the presence of such mixed catalyst two reactions were found to take place simultaneously: (1) polymerization of the olefin hydrocarbon; (2) hydrogenation of the polymer formed. It is suggested that this reaction be called "hydropolymerization."

As is evident from the experiments, magnesium chloride and zinc chloride alone do not act as polymerizing agents under the conditions mentioned. However, in the presence of hydrogenating catalysts, polymerization takes place. It is possible that the energy given off during hydrogenation is sufficient to cause the polymerization of olefins by the weak polymerizing catalyst.

(1) Thus, amylene and isobutene, when treated at 300° and under 80 atm. hydrogen pressure in the presence of reduced iron as catalyst, produced pure pentane and isobutane.

(2) Amylene, under the same conditions, in the presence of magnesium chloride alone did not polymerize.

(3) Amylene and isobutene, under the same conditions, in the presence of a mixed catalyst iron and magnesium chloride containing water, produced decanes and octanes.

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(1) Presented before the Division of Organic Chemistry at the 92nd Meeting of the American Chemical Society in Pittsburgh, Pa., September 7–11, 1936.

(2) Research and Development Laboratories, Universal Oil Products Co., Riverside, Illinois.

(3) Benzene, under similar conditions, could not be hydrogenated (Ipatieff, unpublished results).

(4) V. Ipatieff and A. V. Grosse showed the possibility of hydrogenating the olefins in the presence of aluminum chloride (unpublished work).

(5) V. Ipatieff and V. Komarewsky, unpublished work.

Additional evidence that the reaction of hydro-polymerization is a real simultaneous reaction was given by the fact that when the experiments were conducted under conditions not favorable to the hydrogenation in a glass liner placed in the autoclave, the hydrogenation did not take place even in the presence of a hydrogenation catalyst, and at the same time *no polymerization occurred.*

This paper describes the "hydro-polymerization" of amylene and of isobutene in the presence of the hydrogenating catalysts, reduced iron and nickel oxide, together with the polymerizing agents magnesium, zinc and aluminum chlorides.

Experimental Part

Apparatus and Procedure.—All the experiments were carried out in an electrically heated rotating autoclave of the Ipatieff type (800-cc. capacity). The gaseous products of the reaction were analyzed. The liquid products were fractionated by means of a Podbielniak column.

Experiments with Amylene.—(Trimethylethylene containing methylethylethylene, b. p. 35–37°.)

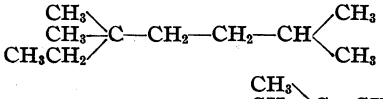
Experiment 1.—Amylene 40.0 g., reduced iron 10.0 g., hydrogen 80 kg./sq. cm., produced at 300° during four hours 32.0 g. of completely saturated (permanganate test) liquid, insoluble in 96% sulfuric acid; b. p. 35°, that of pure isopentane. Gas remaining at the end of the reaction was pure hydrogen.

Experiment 2.—Amylene 40.0 g., reduced iron 10.0 g., magnesium chloride ($MgCl_2 \cdot 6H_2O$) 2.0 g., hydrogen 80 kg./sq. cm., produced at 300° during four hours 30.0 g. of liquid with b. p. 35–173°. The liquid contained only 5% of unsaturated hydrocarbons (96% sulfuric acid treatment). By fractionation of the liquid 10.0 g. of product was obtained which boiled at 170–173° and was completely stable toward permanganate and sulfuric acid.

Anal. Calcd. for $C_{10}H_{22}$: C, 84.51; H, 15.49. Found: C, 84.35; H, 15.63; mol. wt., 140; n^{25}_D 1.4130.

These data show that pure decane was present. Its formation can be explained as the polymerization of two molecules of amylene to its dimer with simultaneous hydrogenation to decane, $2C_5H_{10} + H_2 = C_{10}H_{22}$.

On the basis of the established facts[6] of the polymerization of olefins, we can ascribe to the obtained isodecane the constitution



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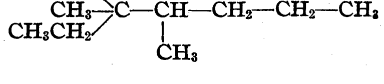


The gas remaining after the reaction contained H, 84%; C_2H_6, 5.1%; C_3H_8, 2%; C_4H_4, 1.0%; CH_4, 8.0%.

Experiment 3.—Forty grams of amylene and 2.0 g. of magnesium chloride heated at 300° during four hours remained unchanged.

Experiment 4.—Amylene (40.0 g.) was unchanged after heating during four hours at 300° with 62.0 g. of reduced iron, 24.6 g. of water and 2.0 g. of magnesium chloride.

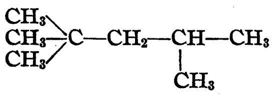
Experiments with Isobutene

Experiment 5.—At 250° under 80 kg./sq. cm. hydrogen pressure in the presence of reduced iron, isobutene hydrogenated to pure isobutane during four hours.

Experiment 6.—Fifty grams of pure isobutene (obtained by dehydration of isobutyl alcohol over activated alumina), 12.5 g. of reduced iron, 2.5 g. of magnesium chloride under 80 kg./sq. cm. of hydrogen produced at 250° during eight hours, 23.0 g. of liquid, b. p. 50–210°, which contained 10% of unsaturated hydrocarbons (sulfuric acid treatment). After the treatment with sulfuric acid (96%) the remaining liquid hydrocarbon was completely stable toward permanganate solution and nitrating mixture. By distillation two fractions were separated: (1) 100–110° and (2) 170–180°. The first fraction had the following properties: n^{25}_D 1.3990; d^{20}_4 0.6970; mol. wt., 110, and octane number, 100.

Anal. Calcd. for C_8H_{18}: C, 84.21; H, 15.79. Found: C, 84.17; H, 15.8.

On the basis of these data the first fraction consisted mainly of isooctane, 2,2,4-trimethylpentane.



The second fraction (b. p. 170–180°) had properties and analysis corresponding to those of an isododecane. The condensable gas (21.5 g.) from the reaction contained 65% of unreacted isobutene and 31.2% of isobutane. The uncondensable gas was pure hydrogen. It is evident that pyrolysis did not take place.

Experiment 7.—The isobutene treated under the same conditions as above but in the presence of magnesium chloride alone did not undergo change.

Experiment 8.—One hundred thirty-five grams of isobutene, 12.5 g. of reduced iron, 5.0 g. of nickel oxide, 5.0 g. of zinc chloride under 80 kg./sq. cm. of hydrogen at 275° during eight hours yielded 109.0 g. of liquid boiling at 32–175° and containing traces of unsaturated hydrocarbons.

Fractionation of this liquid gave 46.5 g. boiling from 100–120° with n^{25}_D 1.3976; d^{20}_4 0.6960; mol. wt., 112.

Anal. Calcd. for C_8H_{18}: C, 84.21; H, 15.79. Found: C, 84.15; H, 15.84.

The gas remaining from the reaction consisted of 92.8% hydrogen and 7.2% isobutane.

Experiment 9.—Isobutene treated under the same conditions but with zinc chloride alone remained unchanged.

Experiment 10.—One hundred and thirty-three grams of isobutene, 10.0 g. of reduced iron, 5.0 g. of nickel oxide and 2.5 g. of aluminum chloride under 80 kg./sq. cm. of hydrogen produced at 275° during twelve hours 115.0 g. of a liquid (b. p. 40–350°) from which 30.0 g. of isoöctane fraction was fractionated which boiled at 100–110°; n^{25}_D 1.4040; d^{20}_4 0.7050; mol. wt., 110.

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(6) V. N. Ipatieff, *Ind. Eng. Chem.*, **27**, 1067 (1935). In this case we have as the catalyst Cl—Mg—OH which forms the ester Cl—Mg—O—C_5H_{11}; and V. N. Ipatieff, "Catalytic Reactions at High Temperatures and Pressures," The Macmillan Co., New York, 1936.

Anal. Calcd. for C_8H_{18}: C, 84.21; H, 15.79. Found: C, 84.10; H, 15.87.

The product isolated was completely stable toward permanganate and nitrating mixture. The yield of isooctane, 2,2,4-trimethylpentane, was less than in some of the other experiments because aluminum chloride is a very strong polymerizing catalyst.

EXPERIMENT 11.—Aluminum chloride alone completely polymerized isobutene under the conditions of the experiments and produced a viscous oil.

Summary

1. A new simultaneous reaction of hydropolymerization was discovered and studied in the case of amylene and isobutene.

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 24, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 568]

The Hydration of Unsaturated Compounds. V. The Rate of Hydration of Acetylene in Aqueous Solution of Sulfuric Acid and Mercuric Sulfate[1]

BY R. H. FRIEMAN,[2] E. R. KENNEDY AND H. J. LUCAS

In the usual commercial process of hydrating acetylene to acetaldehyde in the presence of mercuric sulfate and sulfuric acid, there is present an insoluble or slightly soluble amorphous substance, a mercury organic compound or compounds. It is probable that the composition of these precipitates varies with conditions, as pointed out by Whitmore.[3] As to whether these precipitates are intermediates in the hydration process, the evidence is conflicting. Whitmore points out that the hydration of the triple bond may merely be catalyzed by mercuric ions in acid solution, as in the case of piperonylacetylene.[4] It has been postulated that organo-mercury compounds are intermediates.[5]

The Analytical Method.—The procedure finally developed for the analysis of acetylene in aqueous solution, based upon the methods of Davis, Crandall and Higbee[6] and of Eberz and Lucas[7] follows. Into a 300-ml. conical flask having a ground glass stopper with sealed-in stopcock, is pipetted 25.00 ml. of 0.0500 *N* potassium bromate–bromide solution and the flask is evacuated to about 25 mm. with a water aspirator. Then 5 ml. of 6 *N* sulfuric acid is added, the mixture is allowed to stand for two to three minutes, and then in order are pipetted in, 10 ml. of 0.2 *M* mercuric sulfate, 25 ml. of water, and finally 2 to 10 ml. of the sample to be analyzed, a dilute aqueous solution of acetylene. The last is thoroughly rinsed into the flask from a special pipet of the type described by Eberz and Lucas[7] and the flask, still under vacuum and wrapped in a black cloth to exclude light, is shaken mechanically for five to seven minutes. At this time, 5 ml. of 2.0 *N* sodium chloride and 10 ml. of a freshly prepared 20% potassium iodide solution are added. The shaking is continued for another five to seven minutes, the black cloth is removed, the vacuum is then broken, 50 to 100 ml. of water is added to dilute the solution, and titration is made with 0.03 *N* sodium thiosulfate solution. A blank is run at the same time, omitting only the sample.

Discussion of the Analytical Method.—The simple bromate–bromide method of determining unsaturation is not satisfactory for the triple bond, as pointed out by Davis, Crandall and Higbee[6] in the case of acetylene, because of the interference due to oxygen, and by Mulliken and Wakeman[8] in the case of liquid alkynes, for which the analytical results were low. The former authors showed that aluminum, nickel and mercury salts are an aid in the quantitative determination of acetylene. In the present work it has been found that the bromination of acetylene proceeds rapidly and smoothly if the molal ratio of mercuric sulfate to the total halide present is greater than unity, but under these conditions the iodine end-point with starch is uncertain. The addition of sodium chloride overcomes this difficulty, making reproducible results possible.

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(1) For the preceding paper in this series, see Eberz, Welge, Yost and Lucas, THIS JOURNAL, **59**, 45 (1937).

(2) Mr. Frieman died suddenly of a heart attack on January 13, 1935.

(3) Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., N. Y., 1921, p. 118, cites numerous references.

(4) Manchot and Hass, *Ann.*, **399**, 150 (1913).

(5) Vogt and Nieuwland, THIS JOURNAL, **43**, 2071 (1921); Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **1**, 159 (1936).

(6) Davis, Crandall and Higbee, *Ind. Eng. Chem., Anal. Ed.*, **3**, 108 (1931).

(7) (a) Eberz and Lucas, THIS JOURNAL, **56**, 1232 (1934); (b) Lucas and Eberz, *ibid.*, **56**, 460 (1934).

(8) Mulliken and Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 59 (1935).

The accuracy of the method has been demonstrated by (a) varying the time of bromination, in order to test the possibility of substitution, and (b) varying the ratio of acetylene to bromine in order to determine upper and lower limits. It was found that the same volume of thiosulfate solution was required to back titrate equal volumes of a given aqueous acetylene solution, when the time of bromination was 4, 8, 12, 16, 20 or 24 minutes. This indicates that no substitution takes place. In Fig. 1, in which per cent. of bromine reacted is plotted against the molal ratio of acetylene to bromine, a 45° angle line is drawn, which is the theoretical curve, on the assumption that one-half of the moles of bromine reacted represent the moles of acetylene. An analysis was made of four different aqueous acetylene solutions, in order to establish the acetylene content. These results do not appear on the plot, since they would automatically fall upon the curve. Volumes of the four solutions, different from those taken for the analysis, were then analyzed and the results plotted. It is apparent that the values fall upon the theoretical curve when the initial molal ratio of bromine to acetylene is four or more, *i. e.*, at least twice the theoretical amount, but deviate when this ratio is less. Even when the bromine is in very large excess, *viz.*, one hundred to one, the results are comparable, showing again that no substitution takes place. Because of the good agreement over a wide range of conditions, it is believed that the analytical method is reliable. This procedure of testing the method was resorted to when it was found that pure acetylene was not available, as discussed under purification. The method was not always reliable in the presence of acetaldehyde, as discussed under interference of acetaldehyde.

Materials.—Mercuric sulfate solutions were prepared from C. P. mercuric oxide and C. P. sulfuric acid. Acetaldehyde was prepared by the depolymerization of paraldehyde and was distilled three times through a fractionating column. Solutions of acetaldehyde of known concentration in water were made up by weight. The acetylene was taken from a "Prestolite" cylinder.

Purification of Acetylene.—The acetylene supposedly was purified by passing through solutions in spiral wash bottles, *viz.*, sodium bisulfite, for removing acetone coming from the cylinder, copper sulfate (made acid by the addition of a few drops of sulfuric acid), for removing phosphine, chromic anhydride in 50% (by volume) sulfuric acid, for oxidizing impurities, especially phosphine, and finally sodium hydroxide. The gas then passed through towers packed with solids, *viz.*, calcium chloride, calcium hypochlorite (H. T. H.), and flake sodium hydroxide.[9] The acetylene from this system was still impure for it absorbed more than the theoretical amount of bromine (a variable amount, usually about 114% of the theoretical), its vapor density was 26.60 (against a theoretical value of 26.02), and an aqueous bromine solution, through which a large volume of the gas had been passed, gave a positive phosphomolybdate test for phosphate. Slow passage of the gas through the purifying apparatus enhanced the purity of the gas, for the lowest value of the vapor density, 26.30, was obtained under these conditions. If the per cent. of sulfuric acid in the chromic acid wash bottle was much greater than 50%, there was rather rapid reduction of the chromic acid due to oxidation of the acetylene. Variations in the method of purification, or even a lack of purification, did not alter greatly the bromine value of different samples of gaseous acetylene. The error involved in this determination is 1 to 2% and is due to the difficulty in accurately measuring the small sample of 2 to 3 cc. of gas, and in quantitatively transferring it to the bromine flask.[10] Even though the acetylene contained phosphine, it is believed that the reaction rate data are not influenced by it, since the amount dissolved in the hydrating solutions was so small that a positive phosphomolybdate test could not be obtained.

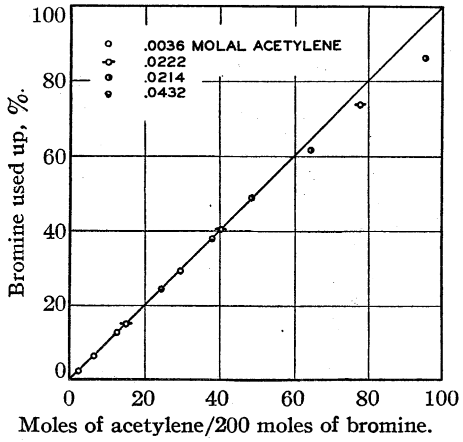

Fig. 1.—Limitations of the analytical method.

Apparatus and Method.—The apparatus previously described[7b] was used for this work. The method consisted in passing acetylene into a sulfuric acid solution of known concentration, 5.000 weight formal (*wf.*),[11] until a sufficient amount was dissolved, and adding a measured volume of standard mercuric sulfate in 5.000 *wf.* sulfuric acid, all at 25°. After shaking, the resulting clear solution[12] was quickly transferred to the apparatus, kept at 25 ± 0.04°, from which samples were removed for analysis at intervals of twenty to forty minutes.

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[9] This train was believed to embody the best features of numerous purification methods described by others. See Mathews, THIS JOURNAL, **22**, 106 (1900); Kahutani and Yamada, *C. A.*, **25**, 1655 (1931); Cummings, Hopper and Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Co., New York, 1931, p. 171; Livingston and Schiflett, *J. Phys. Chem.*, **36**, 750 (1932).

[10] The weight of acetylene was calculated by the use of the *P–V–T* relation given in "International Critical Tables," Vol. III, McGraw-Hill Book Company, Inc., N. Y., 1928, p. 3.

[11] Or 4.167 formula weights per liter (*vf.*).

[12] If any cloudiness developed the liquid was discarded.

Interference of Acetaldehyde with the Analytical Method.—The reaction product, acetaldehyde, interferes with the acetylene analysis. It is not possible to correct for this effect, because of the variability of results when aldehyde solutions are added to the analytical mixture. There appeared to be a qualitative relationship between the amount of bromine used up and the age of the added aldehyde solution; moreover, this amount appeared to increase more rapidly as the concentration of the acid was raised. It is probable that the variations in the amount of bromine used up by added acetaldehyde, which in some cases were as much as 100%, were due to its partial conversion to other products, such as paraldehyde, aldol and crotonic aldehyde. The error due to the interference of aldehyde with the analytical procedure was estimated to be of the same order of magnitude as the precision of measurement by the time the acetylene was about one-fourth reacted. In the initial stages of the hydration, where the concentration of aldehyde (and consequently the bromine reactive substance) was very small, the analytical procedure was regarded as reliable.

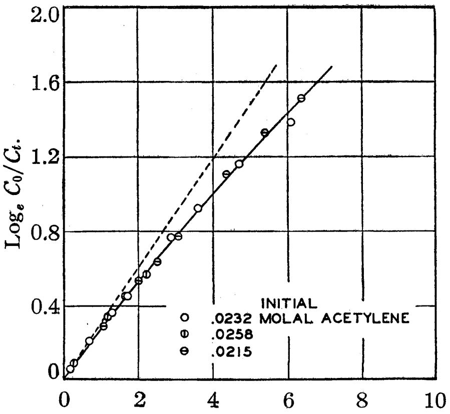

Fig. 2.—Hydration of acetylene in 5.00 weight formal sulfuric acid and 5.00 × 10^{-5} weight formal mercuric sulfate.

The Initial Hydration Rate.—In order to obtain the initial slope of $\log_e C_0/C_t$ against t (in hours), it was necessary to extrapolate to zero time. The data and the initial slopes of fourteen experiments are shown in Table I. When the mercuric sulfate is 5.00 × 10^{-5} *wf.*, and when no aldehyde has been added, the values of the initial reaction rate constants (taken from the initial slopes) lie between 0.285 and 0.322, with 0.290 as the average. The satisfactory agreement here, over a five-fold change in initial acetylene concentration, shows that the initial rate is first order with respect to the acetylene concentration. The similarity of different runs is shown by plotting $\log_e C_0/C_t$ against t, as in Fig. 2, which gives the results of three typical experiments, *viz.*, 4, 5 and 6. Here the data of all three fall upon the solid curve; the dotted straight line is the average initial slope of eight experiments. It is evident that the rate subsequent to the initial one does not obey the first order equation, but apparently is dependent upon some higher power, which proved to be the four-thirds power.

Table I

Hydration Experiments in 5.00 Weight-Formal Sulfuric Acid

Run	k initial, hrs.$^{-1}$	Initial concentration C_2H_2 *vf.*	CH_3CHO *vf.*	$HgSO_4$ *wf.* × 10^5
1	0.292	0.0225	zero	5.00
2	.285	.0252	zero	5.00
4	.302	.0232	zero	5.00
5	.288	.0215	zero	5.00
6	.285	.0285	zero	5.00
7	.260	.0123	zero	5.00
13	.322	.0052	zero	5.00
14	.293	.0245	zero	5.00
Average	.290			
3	.186	.0229	zero	4.00
10	.415	.0275	zero	6.00
9	zero	.0470	zero	zero
8	.201	.0257	0.042	5.00
11	.198	.0248	.083	5.00
12	.285	.0275	.083	6.00

The initial hydration rate is second order with respect to the concentration of mercuric sulfate, for the plot of the initial rate constant against the square of the mercuric sulfate concentration gives a straight line, as shown in Fig. 3. This must pass through the origin, because sulfuric acid alone, in the absence of mercuric sulfate, did not cause hydration of acetylene. It is worthy of note that dependence of rate upon the square of the mercuric sulfate holds when aldehyde is present (experiments 11 and 12, Table I).

The dependence of the rate upon the concentration of the sulfuric acid was not studied. The rate appears to be dependent upon a higher than first power acid concentration because, in 1 *wf.* sulfuric acid (0.963 *vf.*), the hydration proceeds too slowly to be measured.

The Effect of Acetaldehyde upon the Hydration Rate.—The apparent four-thirds power relationship between the reaction rate constant during the course of the hydration, and the acetylene concentration, a relationship which is true of experiments 4, 5 and 6, held in some other cases.

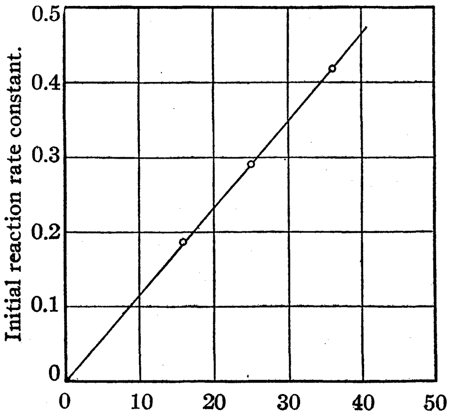

Fig. 3.—Relationship of initial rate constant to the concentration of mercuric ion.

However, it is not typical of all the experiments, for example, those in which the initial acetylene concentration was low (7 and 13) and those in which recently distilled aldehyde was added (8, 11 and 12). Figure 4, in which is plotted the curve for experiment 8 (solid line), indicates a first power relationship to the acetylene. However, the slope of this line is below the value when no aldehyde has been added, shown by the broken line. The effect is not due to interference with the analytical procedure, for the time hardly permitted the formation of the substance responsible for the interference. On the other hand, erratic data and no smooth curves resulted when aldehyde solutions in sulfuric acid which had stood for two to three days, were used instead of a freshly prepared solution. There was no dependence upon the first power relationship in these cases. Since erratic results were associated with some runs in which freshly prepared aldehyde solution was added (for instance, the constants are practically identical in experiments 8 and 11, in which the initial aldehyde concentrations differed by a factor of 2), the best basis for considering the effect of acetaldehyde lies with those experiments which had no acetaldehyde originally. Assuming that the acetaldehyde concentration at the time, *t*, is given by the acetylene which has undergone hydration up to that time, the rate varies approximately as the inverse three-halves power of the aldehyde concentration in those experiments in which the four-thirds power relationship to acetylene held.

The four-thirds power dependence of the rate upon the acetylene concentration, characteristic of such runs, the apparent inverse three-halves power relationship to acetaldehyde concentration, the drop in the initial rate constant when aldehyde is added initially, and the first power relationship of the rate to acetylene concentration under these conditions, probably depend upon the formation of a complex between mercuric ion and acetaldehyde.[13,14]

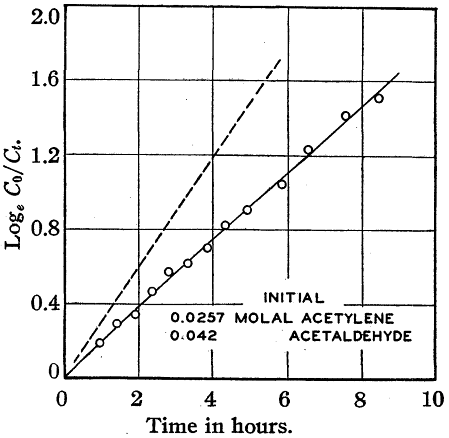

Fig. 4.—Influence of added acetaldehyde upon the hydration of acetylene.

Discussion of the Hydration Mechanism.—Since the homogeneous hydration rate of acetylene is first order with respect to the acetylene concentration, and second order with respect to the mercuric sulfate (or acid sulfate) concentration, the simplest interpretation of the reaction mechanism is the assumption that an intermediate complex, from one molecule of acetylene and two molecules of mercuric sulfate (or bisulfate), is the substance which undergoes hydration:

$$C_2H_2 + 2Hg(HSO_4)_2 \rightleftharpoons C_2H_2Hg_2(HSO_4)_4$$

$$C_2H_2Hg_2(HSO_4)_4 + H_2O + nH_3O^+ \longrightarrow CH_3CHO + 2Hg(HSO_4)_2 + nH_3O^+$$

It is probable that mercuric bisulfate is the reactive substance, since in the strongly acid solution bisulfate ions predominate over sulfate ions. The assumed higher than first power dependence of the hydration rate upon sulfuric acid is in part accounted for by the presence of the two bisulfate radicals in the complex. Because of the additional catalytic effect of hydrogen ion,

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(13) Denigès, *Ann. chim. phys.*, [7] **18**, 396 (1899), describes a compound of mercuric sulfate and acetaldehyde, $CH_3CHO \cdot HgSO_4 \cdot 2HgO$, which is destroyed by hydrochloric acid with regeneration of the aldehyde.

(14) The referee has suggested that the effect may be due to the fact that mercuric ion suffers reduction in the presence of oxygen.

one might reasonably expect a third power, or even higher, dependence. The importance of bisulfate ion in the hydration of acetylene is shown by the work of Vogt and Nieuwland,[5] whose best catalytic mixtures were saturated solutions of potassium (or similar) bisulfate in contact with mercuric sulfate.

One could propose a plausible mechanism for the hydration reaction, based upon the above equation, but the information at present available is still insufficient to permit of a definite decision.

Summary

Acetylene undergoes homogeneous hydration to acetaldehyde in aqueous solutions in the presence of mercuric sulfate and sulfuric acid. The initial rate of hydration is first order with respect to the acetylene concentration and second order with respect to the mercuric sulfate concentation, while the rate at time *t* has an apparent four-thirds power dependence upon the acetylene. This last is believed to result from the formation of a complex between mercuric sulfate and acetaldehyde.

A probable mechanism of the hydration involves the formation of an intermediate complex between one molecule of acetylene and two molecules of mercuric bisulfate, and the reaction of this complex with water, in the presence of an acid, to form vinyl alcohol, which rearranges to acetaldehyde.

The bromate–bromide method of determining unsaturation is applicable to aqueous solutions of acetylene, provided there is present a soluble mercuric salt whose molal ratio to total halide is greater than unity.

PASADENA, CALIF. RECEIVED NOVEMBER 30, 1936

[CONTRIBUTION FROM THE BURROUGHS WELLCOME AND CO., U. S. A., EXPERIMENTAL RESEARCH LABORATORIES]

Pharmacologically Active Compounds from Alkoxy-β-phenylethylamines

BY WALTER S. IDE AND JOHANNES S. BUCK

Considerable pharmacological data have been accumulated on compounds connected with or prepared from methoxy-β-phenylethylamines. It is therefore of great interest to examine the corresponding ethoxy compounds, for this would allow an exact comparison of the pharmacological effects of the ethoxy and methoxy groups to be made. The authors have therefore prepared seven such β-phenylethylamines and from them several series of compounds (N-methylamines, ureas, *unsym*-methylureas, barbituric acids, isoquinolines, N-methylisoquinolines, benzyl-β-phenylethylamines, and characterizing compounds).

Experimental

The amines were prepared by the series of reactions used by Buck.[1,2] As starting materials aldehydes with the following substituents were used (hereafter these letters refer to the same substituents):

A 2-Ethoxy-
B 3-Ethoxy-
C 4-Ethoxy-
D 2-Ethoxy-3-methoxy-
E 3-Methoxy-4-ethoxy-
F 3-Ethoxy-4-methoxy-
G 3,4-Diethoxy-

The aldehydes A, B, C, D and E were prepared by ethylating (ethyl sulfate and sodium hydroxide) the corresponding phenolic aldehydes. Aldehyde F was prepared by methylating 3-ethoxy-4-hydroxybenzaldehyde and aldehyde G by ethylating the same phenolic aldehyde.

The aldehydes, together with a number of intermediates, have been described previously (see references, where *Cf.* indicates a different method of preparation or an indirect reference). New intermediates are given in the table.

References on Intermediates

Aldehydes

A *Cf.* Perkin, *Ann.*, **145**, 306 (1868); Löw, *Monatsh.*, **12**, 396 (1892).
B *Cf.* Werner, *Ber.*, **28**, 2001 (1895); Subak, *Monatsh.*, **24**, 169 Note (1904).
C *Cf.* Kostanecki and Schneider, *Ber.*, **29**, 1892 Note (1896); Hildesheimer, *Monatsh.*, **22**, 499 Note (1902); Gattermann, *Ber.*, **31** 1151 (1898); *Ann.*, **357**, 347 (1907).
D *Cf.* Davies and Rubenstein, *J. Chem. Soc.*, **123**, 2846 (1923).
E, F, G. Buck and Ide, THIS JOURNAL, **54**, 3302 (1932).

Cinnamic Acids

A *Cf.* Perkin, *J. Chem. Soc.*, **39**, 413 (1881); Fittig and Ebert, *Ann.*, **216**, 146 (1883); Stoermer, *Ber.*, **44**, 645 (1911).
B *Cf.* Werner, *loc. cit.*
C *Cf.* Stoermer and Wodarg, *Ber.*, **44**, 637 (1911).
D Rubenstein, *J. Chem. Soc.*, 652 (1926).
E Schlittler, *Ber.*, **66**, 988 (1933); Slotta and Heller, *ibid.*, **63**, 3029 (1930).

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[1] Buck, THIS JOURNAL, **54**, 3661 (1932).
[2] Buck, *ibid.*, **52**, 4119 (1930).

TABLE I

NEW INTERMEDIATES

Substituent	Compound	Appearance	M. p., °C.	Formula	N Analyses, % Calcd. C	H	Found C	H
G	3,4-Diethoxycinnamic acid[a]	Glitt. flakes	156	$C_{13}H_{16}O_4$	66.07	6.83	66.07	7.05
D	2-Ethoxy-3-methoxyphenylpropionic acid[b]	Large hard prisms	65	$C_{12}H_{16}O_4$	64.25	7.20	64.07	7.50
A	2-Ethoxyphenylpropionamide[c]	Felted needles	106	$C_{11}H_{15}O_2N$	68.35	7.83	68.15	8.10
B	3-Ethoxyphenylpropionamide[c]	Felted needles	80	$C_{11}H_{15}O_2N$	68.35	7.83	68.52	8.19
C	4-Ethoxyphenylpropionamide[c]	Felted needles	137	$C_{11}H_{15}O_2N$	68.35	7.83	68.66	8.15
D	2-Ethoxy-3-methoxyphenylpropionamide[c]	Large hard prisms	85	$C_{12}H_{17}O_3N$	64.53	7.68	64.38	7.86

[a] Moderately soluble in alcohol and benzene; sparingly soluble in ether and petroleum ether; insoluble in water. Recrystallized from alcohol–ether.

[b] Soluble in alcohol, benzene and ether; insoluble in petroleum ether and water; melts in hot water. Final solvent aqueous alcohol.

[c] Moderately to sparingly soluble in benzene, ethyl acetate, alcohol and water; insoluble in ether and petroleum ether. Final solvent benzene, washing with petroleum ether.

TABLE II

ALKOXY-β-PHENYLETHYLAMINES

Substituent	B. p. °C.	Mm.	n^{25}_D	d^{25}_4	M_D	Formula	N Analyses, % Calcd.	Found
A	128–130	13	1.5278	1.0091	50.37[a]	$C_{10}H_{15}ON$	8.48	8.36
B	135–138	13	1.5281	1.0082	50.44[a]	$C_{10}H_{15}ON$	8.48	8.44
C	138–140	13	1.5325	1.0084	50.78[a]	$C_{10}H_{15}ON$	8.48	8.65
D	148–150	13	1.5286	1.0519	57.18[b]	$C_{11}H_{17}O_2N$	7.17	7.13
E[3]	160	13	1.5393	1.0661	57.37[b]	$C_{11}H_{17}O_2N$	7.17	7.41
F[3]	168	15	1.5376	1.0646	57.29[b]	$C_{11}H_{17}O_2N$	7.17	7.08
G[4]	158	13	1.5270	1.0366	61.89[c]	$C_{12}H_{19}O_2N$	6.69	6.83
ALKOXY-β-PHENYLETHYLMETHYLAMINES								
A	97	2	1.5142	0.9773	55.20[d]	$C_{11}H_{17}ON$	7.82	8.06
B	106	2	1.5157	.9791	55.24[d]	$C_{11}H_{17}ON$	7.82	7.66
C	107	2	1.5154	.9792	55.21[d]	$C_{11}H_{17}ON$	7.82	7.68
D	119	1.5	1.5146	1.0225	61.64[e]	$C_{12}H_{19}O_2N$	6.69	6.90
E	128	1.5	1.5275	1.0420	61.75[e]	$C_{12}H_{19}O_2N$	6.69	6.91
F	129	1.5	1.5234	1.0319	61.95[e]	$C_{12}H_{19}O_2N$	6.69	6.77
G	129	2	1.5146	1.0081	66.71[f]	$C_{13}H_{21}O_2N$	6.27	6.41

[a] Calcd. (Brühl) = 50.03

[b] Calcd. (Brühl) = 56.31

[c] Calcd. (Brühl) = 60.92

[d] Calcd. (Brühl) = 54.83

[e] Calcd. (Brühl) = 61.12

[f] Calcd. (Brühl) = 65.72

F Schlittler, *loc. cit.*
G See table.

Phenylpropionic (Hydrocinnamic) Acids

A *Cf.* Fittig and Ebert, *loc. cit.*, p. 153; Fittig and Claus, *Ann.*, **269**, 12 (1892).
B Bayer and Company, German Patent 234,852.
C *Cf.* Bougault, *Ann. chim. phys.*, [7] **25**, 505 (1902).
D See table.
E Schlittler, *loc. cit.*; Slotta and Heller, *loc. cit.*
F *Cf.* Schlittler, *loc. cit.*
G *Cf.* Kindler and Peschke, *Arch. Pharm.*, **272**, 60 (1934).

Amides

A, B, C, D. See table.
E Schlittler, *loc. cit.*, Slotta and Heller, *loc. cit.*
F Schlittler, *loc. cit.*
G Kindler and Peschke, *loc. cit.*

Alkoxy-β-phenylethylamines.—These were prepared from the corresponding amide by a Hofmann reaction, using sodium hypochlorite. They are colorless liquids, insoluble in water, and having a faint musty odor when freshly distilled. After standing they smell of ammonia. They form solid carbonates very readily in the air.

Alkoxy-β-phenylethylmethylamines are prepared from the above amines by the Decker method, through the Schiff base and methyl iodide, as described by Buck.[1,2] The amines are colorless liquids, sparingly soluble in water and having a faint musty odor. They do not form solid carbonates as readily as the primary amines. The Schiff bases were not isolated at this point. The hydriodides are soluble in water and alcohol. They were recrystallized from alcohol–ether mixture.

Alkoxy-β-phenylethylamine hydrochlorides were prepared either from the amines by dissolving them in absolute alcohol and passing in dry hydrogen chloride, after which they were recrystallized from alcohol–ether mixture, or by the use of silver chloride on the hydriodides. They are very soluble in cold water, soluble in cold alcohol, spar-

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(3) Slotta and Heller, *loc. cit.*, Schlittler, *loc. cit.*, *cf.* Späth and Dobrowsky, *Ber.*, **58**, 1274 (1925).

(4) *Cf.* Slotta and Haberland, *Z. angew. Chem.*, **46**, 766 (1933); Kindler and Peschke, *loc. cit.*

TABLE III

ALKOXY-β-PHENYLETHYLMETHYLAMINE HYDRIODIDES

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	Faint yellow felted needles	118	$C_{11}H_{18}ONI$	4.56	4.44
B	Glittering flakes	74	$C_{11}H_{18}ONI$	4.56	4.51
C	Faint yellow tiny flakes	129	$C_{11}H_{18}ONI$	4.56	4.65
D	Faint yellow rosets of prisms	122	$C_{12}H_{20}O_2NI$	4.15	4.07
E	Faint yellow tiny flakes	228	$C_{12}H_{20}O_2NI$	4.15	4.04
F	Yellow tiny flakes	154	$C_{12}H_{20}O_2NI$	4.15	4.05
G	Faint yellow tiny flakes	100	$C_{13}H_{22}O_2NI$	3.99	3.93

TABLE IV

ALKOXY-β-PHENYLETHYLAMINE HYDROCHLORIDES

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A[5]	Felted needles	218	$C_{10}H_{16}ONCl$	6.95	7.18
B[5]	Glitt. leaves	Jells at 146, flows at 168	$C_{10}H_{16}ONCl$	6.95	7.26
C[5]	Glitt. plates	206	$C_{10}H_{16}ONCl$	6.95	7.13
D	Glitt. plates	162	$C_{11}H_{18}O_2NCl$	6.04	6.18
E[6]	Tiny needles	168	$C_{11}H_{18}O_2NCl$	6.04	5.98
F[6]	Fine needles	168	$C_{11}H_{18}O_2NCl$	6.04	6.10
G[7]	Fine needles	Jells at 144, flows at 198	$C_{12}H_{20}O_2NCl$	5.70	5.80

ALKOXY-β-PHENYLETHYLMETHYLAMINE HYDROCHLORIDES

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	Felted needles	133	$C_{11}H_{18}ONCl$	6.49	6.80
B	Glitt. flakes	144	$C_{11}H_{18}ONCl$	6.49	6.59
C	Glitt. flakes	206	$C_{11}H_{18}ONCl$	6.49	6.61
D	Glitt. flakes	147	$C_{12}O_{20}O_2NCl$	5.70	5.89
E	Glitt. flakes	131	$C_{12}H_{20}O_2NCl$	5.70	5.90
F	Felted needles	159	$C_{12}H_{20}O_2NCl$	5.70	5.96
G	Felted needles	157	$C_{13}H_{22}O_2NCl$	5.39	5.58

ingly soluble in ether and ethyl acetate and readily soluble in cold concentrated hydrochloric acid.

Alkoxy-β-phenylethylmethylamine hydrochlorides were prepared as above. Their solubilities are practically the same.

TABLE V

ALKOXY-β-PHENYLETHYLUREAS

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	White powder	112	$C_{11}H_{16}O_2N_2$	13.45	13.49
B	Glitt. leaves	104	$C_{11}H_{16}O_2N_2$	13.45	13.46
C	Glitt. leaves	134	$C_{11}H_{16}O_2N_2$	13.45	13.46
D	Felted needles	120	$C_{12}H_{18}O_3N_2$	11.76	11.80
E	Felted needles	126	$C_{12}H_{18}O_3N_2$	11.76	11.67
F	Felted needles	145	$C_{12}H_{18}O_3N_2$	11.76	11.69
G	Felted needles	108	$C_{13}H_{20}O_3N_2$	11.10	11.18

ALKOXY-β-PHENYLETHYLMETHYLUREAS

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	White powder	84	$C_{12}H_{18}O_2N_2$	12.60	12.82
B	Glitt. prisms	118	$C_{12}H_{18}O_2N_2$	12.60	12.86
C	Glitt. leaves	149	$C_{12}H_{18}O_2N_2$	12.60	12.80
D	White powder	76	$C_{13}H_{20}O_3N_2$	11.10	11.12
E	Tiny flakes	112	$C_{13}H_{20}O_3N_2$	11.10	11.02
F	White powder	96	$C_{13}H_{20}O_3N_2$	11.10	11.07
G	Tiny flakes	97	$C_{14}H_{22}O_3N_2$	10.52	10.70

Alkoxy-β-phenylethylureas and *unsym*-methylureas were prepared by using the nitrourea method as described earlier.[8–11] They are moderately soluble in benzene and alcohol, sparingly soluble in petroleum ether. Urea D was also prepared by the potassium cyanate method but the product requires more treatment.

1-(Alkoxy-β-phenylethyl)-5,5-diethyl Barbituric Acids.—The barbituric acids were prepared from the corresponding ureas by a method described by Buck.[8,12,13] B and C reaction mixtures were diluted and made acid to Congo red. The product separated as an oil and soon solidified. In the case of A, D, E, F, G, the reaction mix-

TABLE VI

1 - (ALKOXY - β - PHENYLETHYL) - 5,5 - DIETHYLBARBITURIC ACIDS

Alkoxy substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	White powder	66	$C_{18}H_{24}O_4N_2$	8.43	8.53
B	Tiny flakes	86	$C_{18}H_{24}O_4N_2$	8.43	8.49
C	Large prisms	134	$C_{18}H_{24}O_4N_2$	8.43	8.69
D	Small prisms	68	$C_{19}H_{26}O_5N_2$	7.73	7.75
E	Tiny needles	120	$C_{19}H_{26}O_5N_2$	7.73	7.78
F	White powder	99	$C_{19}H_{26}O_5N_2$	7.73	7.97
G	Large prisms	88	$C_{20}H_{28}O_5N_2$	7.44	7.54

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(5) Bayer and Company, German Patent, 233,551, 233,069.

(6) Sawai, *J. Pharm. Soc. Japan*, **49**, 48 (1929); *cf.* Kondo, *et al.*, *ibid.*, **48**, 169 (1928).

(7) Slotta and Haberland, *loc. cit.*; Kindler and Peschke, *loc. cit.*, give m. p. 195°, sintering above 130°.

(8) Buck, THIS JOURNAL, **56**, 1607 (1934).

(9) Davis and Blanchard, *ibid.*, **51**, 1790 (1929).

(10) Buck and Ferry, *ibid.*, **58**, 854 (1936).

(11) Buck, Hjort and deBeer, *J. Pharmacol.*, **54**, 188 (1935).

(12) Buck, THIS JOURNAL, **58**, 1284 (1936).

(13) Buck, *ibid.*, **58**, 2059 (1936).

ture was treated as described in the above references. A and D were especially difficult to obtain crystalline. Both were distilled at 1 mm. (*ca.* 212 and 225°). Many months at 0° in hexane were necessary to obtain seeding crystals. The barbituric acids are moderately soluble in hexane, soluble in alcohol and ether. They are best re-

TABLE VII

BENZYL-(ALKOXY-β-PHENYLETHYL)-AMINE HYDROCHLORIDES

Phenylethyl substituent	Benzyl substituent	Appearance	M. p., °C.	Formula	N Analyses, %	
					Calcd.	Found
A	Unsubst.	White powder	122	$C_{17}H_{22}ONCl$	4.80	4.77
A	A	Hard prisms	153	$C_{19}H_{26}O_2NCl$	4.17	4.14
A	B	Crusts of prisms	113	$C_{19}H_{26}O_2NCl$	4.17	4.46
A	C	White powder	134	$C_{19}H_{26}O_2NCl$	4.17	4.24
A	G	Tiny flakes	148	$C_{21}H_{30}O_3NCl$	3.69	3.91
B	Unsubst.	Short prisms	194	$C_{17}H_{22}ONCl$	4.80	4.91
B	A	Needles	135	$C_{19}H_{26}O_2NCl$	4.17	4.44
B	B	Glitt. flakes	146	$C_{19}H_{26}O_2NCl$	4.17	4.30
B	C	Glitt. tiny flakes	195	$C_{19}H_{26}O_2NCl$	4.17	4.27
B	G	Glitt. white powder	114	$C_{21}H_{30}O_3NCl$	3.69	3.73
C	Unsubst.	Large silvery flakes	240	$C_{17}H_{22}ONCl$	4.80	5.02
C	A	Crusts of prisms	143	$C_{19}H_{26}O_2NCl$	4.17	4.37
C	B	Glitt. flakes	167	$C_{19}H_{26}O_2NCl$	4.17	4.36
C	C	Needles	280	$C_{19}H_{26}O_2NCl$	4.17	4.26
C	G	White powder	186	$C_{21}H_{30}O_3NCl$	3.69	3.68
D	Unsubst.	Hard gray rhombs	162	$C_{18}H_{24}O_2NCl$	4.35	4.39
D	A	Small prisms	168	$C_{20}H_{28}O_3NCl$	3.83	4.05
D	B	Needles	124	$C_{20}H_{28}O_3NCl$	3.83	3.93
D	C	White powder	120	$C_{20}H_{28}O_3NCl$	3.83	3.96
D	G	White powder	113	$C_{22}H_{32}O_4NCl$	3.42	3.56
E	Unsubst.	Felted needles	200	$C_{18}H_{24}O_2NCl$	4.35	4.30
E	A	White powder	128	$C_{20}H_{28}O_3NCl$	3.83	4.02
E	B	White powder	106	$C_{20}H_{28}O_3NCl$	3.83	4.08
E	C	Needles	239	$C_{20}H_{28}O_3NCl$	3.83	3.96
E	G	White powder	154	$C_{22}H_{32}O_4NCl$	3.42	3.49
F	Unsubst.	Tiny needles	195	$C_{18}H_{24}O_2NCl$	4.35	4.48
F	A	Glitt. leaves	174	$C_{20}H_{28}O_3NCl$	3.83	4.06
F	B	Fine cryst.	103	$C_{20}H_{28}O_3NCl$	3.83	4.10
F	C	Tiny needles	218	$C_{20}H_{28}O_3NCl$	3.83	4.13
F	G	White cryst. powder	122	$C_{22}H_{32}O_4NCl$	3.42	3.62
G	Unsubst.	Felted needles	190	$C_{19}H_{26}O_2NCl$	4.17	4.23
G	A	Cryst. powder	168	$C_{21}H_{30}O_3NCl$	3.69	3.95
G	B	Felted needles	104	$C_{21}H_{30}O_3NCl$	3.69	3.81
G	C	Glitt. leaves	208	$C_{21}H_{30}O_3NCl$	3.69	3.92
G	G	Silvery flakes	112	$C_{23}H_{34}O_4NCl$	3.30	3.35
		BENZYL-(ALKOXY-β-PHENYLETHYL)-AMINES				
A	A	Felted needles	133	$C_{19}H_{25}O_2N$	4.69	4.73
E	C	Tiny plates	78	$C_{20}H_{27}O_3N$	4.25	4.25
E	G	Tiny plates	92	$C_{22}H_{31}O_4N$	3.75	3.78
G	C	Prisms	105	$C_{21}H_{29}O_3N$	4.08	4.16
G	G	Tiny glitt. plates	98	$C_{23}H_{33}O_4N$	3.62	3.63
		BENZYLIDENE-(ALKOXY-β-PHENYLETHYL)-AMINES				
C	C	Large rhombs	90	$C_{19}H_{23}O_2N$	4.71	4.68
C	G	Platelets	86	$C_{21}H_{27}O_3N$	4.10	4.15
F	A	Rhombs	66	$C_{20}H_{25}O_3N$	4.28	4.26
E	Unsubst.	Faint yellow needles	67	$C_{18}H_{21}O_2N$	4.94	5.23
E	C	Glitt. leaves	107	$C_{20}H_{25}O_3N$	4.28	4.33
E	G	Glitt. leaves	115	$C_{22}H_{29}O_4N$	3.76	3.89
F	G	Tiny needles	96	$C_{22}H_{29}O_4N$	3.76	3.89
G	C	Glitt. small prisms	96	$C_{21}H_{27}O_3N$	4.10	4.19
G	G	Glitt. plates	122	$C_{23}H_{31}O_4N$	3.63	3.70
F	C	Faint yellow flakes	60	$C_{20}H_{25}O_3N$	4.28	4.37
G	A	Hard cream prisms	52	$C_{21}H_{27}O_3N$	4.10	4.09

TABLE VIII

ALKOXYTETRAHYDROISOQUINOLINE HYDROCHLORIDES

Amine substituent	Compound	Appearance	M. p., °C.	Formula	N Analyses, %	
					Calcd.	Found
A	5-Ethoxy					
B	6-Ethoxy	White cryst. powder	251	$C_{11}H_{16}ONCl$	6.55	6.74
C	7-Ethoxy					
D	5-Ethoxy-6-methoxy	Glitt. small leaves	184	$C_{12}H_{18}O_2NCl$	5.74	5.84
E	6-Methoxy-7-ethoxy[16]	Tiny needles	284	$C_{12}H_{18}O_2NCl$	5.74	5.74
F	6-Ethoxy-7-methoxy	Tiny needles	282	$C_{12}H_{18}O_2NCl$	5.74	5.71
G	6,7-Diethoxy	Tinted flakes	268	$C_{13}H_{20}O_2NCl$	5.43	5.57

ALKOXY-N-METHYLTETRAHYDROISOQUINOLINE HYDROCHLORIDES

Amine substituent	Compound	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	5-Ethoxy					
B	6-Ethoxy	White powder	froth at 144, dec. at 220	$C_{12}H_{18}ONCl$	7.03	7.14
C	7-Ethoxy					
D	5-Ethoxy-6-methoxy	White powder	220	$C_{13}H_{20}O_2NCl$	5.43	5.33
E	6-Methoxy-7-ethoxy	Tinted flakes	270	$C_{13}H_{20}O_2NCl$	5.43	5.71
F	6-Ethoxy-7-methoxy	White powder	208	$C_{13}H_{20}O_2NCl$	5.43	5.59
G	6,7-Diethoxy	White powder	198	$C_{14}H_{22}O_2NCl$	5.15	5.28

TABLE IX

4-NITROBENZOYL-(ALKOXY-β-PHENYLETHYL)-AMINES

Substituent	Appearance	M. p., °C.	Formula	N Analyses, %	
				Calcd.	Found
A	Tiny white prisms	120	$C_{17}H_{18}O_4N_2$	8.91	8.89
B	Tiny white prisms	113	$C_{17}H_{18}O_4N_2$	8.91	9.03
C	Tiny white prisms	154	$C_{17}H_{18}O_4N_2$	8.91	8.97
D	Felted white needles	102	$C_{18}H_{20}O_5N_2$	8.13	8.20
E	Bright yellow needles	157	$C_{18}H_{20}O_5N_2$	8.13	8.28
F	Bright yellow needles	156	$C_{18}H_{20}O_5N_2$	8.13	8.35
G	Yellow felted needles	138	$C_{19}H_{22}O_5N_2$	7.82	7.98

4-NITROBENZOYL-(ALKOXY-β-PHENYLETHYL)-METHYLAMINES

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	Faint yellow felted needles	235	$C_{18}H_{20}O_4N_2$	8.53	8.45
B	Faint yellow felted needles	222	$C_{18}H_{20}O_4N_2$	8.53	8.73
C	White felted needles	118	$C_{18}H_{20}O_4N_2$	8.53	8.49
D	Faint yellow fine prisms	78	$C_{19}H_{22}O_5N_2$	7.82	7.97
E	Bright yellow needles	155	$C_{19}H_{22}O_5N_2$	7.82	7.99
F	Faint yellow glitt. leaves	102	$C_{19}H_{22}O_5N_2$	7.82	7.96
G	Large clear prisms	58	$C_{20}H_{24}O_5N_2$	7.52	7.41

crystallized by taking up in a little absolute alcohol–ether mixture from which the crystals separate on evaporation of the solvent.

Benzyl-(alkoxy-β-phenylethyl)-amine Hydrochlorides.—These were prepared by condensing the amine with the appropriate aldehyde to form the Schiff bases and reducing these by the Adams method.[14] While no attempt was made to isolate the Schiff bases, a number of these separated on removing water from the reaction mixture and are recorded. A few amines were obtained solid and are recorded but the majority were converted directly into the hydrochloride by the addition of concentrated hydrochloric acid. The amines are rather soluble in the ordinary solvents. A small amount of absolute alcohol–ether mixture was found best for recrystallization. The hydrochlorides are in general moderately soluble in alcohol and benzene, sparingly soluble in hot water, ether and petroleum ether.

Alkoxytetrahydroisoquinoline and N-Methyltetrahydroisoquinoline Hydrochlorides.—The hydrochlorides were prepared by treating the corresponding amines with 40% formalin and then cyclizing the product with hydrochloric acid, as described elsewhere.[15] In line with previous experience it was found that, unless a substituent (alkoxy) was present meta to the side-chain of the amine, cyclization did not proceed normally under the conditions used.[16] The two series of hydrochlorides show little difference. They are readily soluble in cold water, moderately soluble in cold absolute alcohol, sparingly soluble in ether and ethyl acetate, and readily soluble in cold concd. hydrochloric acid.

4 - Nitrobenzoyl - (alkoxy - β - phenylethyl) - amines and N-Methylamines.—The 4-nitrobenzoyl compounds were prepared by treating the amine hydrochloride in benzene with 4-nitrobenzoyl chloride.[17] After heating for a short time the benzene was evaporated and the solid residue further heated on the steam-bath. The compound was taken up in a little benzene, shaken with dilute potas-

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(14) Buck, THIS JOURNAL, **53**, 2192 (1931).

(15) Buck, *ibid.*, **56**, 1769 (1934).

(16) Kondo and Tanaka, *J. Pharm. Soc. Japan*, **49**, 4 (1929).

(17) Buck, THIS JOURNAL, **55**, 2593 (1933).

sium hydroxide, and washed with water, and further purified by recrystallizing from alcohol. They are insoluble in water and moderately soluble in alcohol.

The amines, N-methylamines, benzylphenylethylamines, isoquinolines and N-methylisoquinolines were not O-dealkylated as the corresponding hydroxy derivatives required for the pharmacological work have been prepared previously by demethylating the appropriate methoxy derivatives.[1,2,14,15]

The pharmacological work will be reported in another place. Some of that previously done is reported elsewhere.[11,18-21]

Nitrogen determinations were carried out by a micro-Dumas method. Melting points are corrected.

Summary

A series of seven alkoxy-β-phenylethylamines has been prepared, and from these amines the corresponding N-methylamines, ureas, *unsym*-methylureas, barbituric acids, isoquinolines, N-methylisoquinolines, benzyl-β-phenylethylamines and characterizing compounds have been made. Over one hundred and twenty of these compounds have not been described previously.

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[18] Hjort, *J. Pharmacol.*, **50**, 131 (1934).

[19] Hjort, deBeer, Buck and Ide, *ibid.*, **55**, 152 (1935).

[20] Hjort, *ibid.*, **52**, 101 (1934).

[21] DeBeer and Hjort, *ibid.*, **52**, 211 (1934).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of the Conductance of Electrolytes.[1,2] VIII. A Redetermination of the Conductance of Kohlrausch's Standard Potassium Chloride Solutions in Absolute Units

BY GRINNELL JONES AND MAURICE JOSEPH PRENDERGAST

Most of the experimenters who have measured the electrical conductance of solutions have calibrated their cells by means of either a 1 or 0.1 or 0.01 N solution of potassium chloride whose absolute conductance was assumed to be known from the measurements of Kohlrausch, Holborn and Diesselhorst.[3] Unfortunately, Kohlrausch gives alternative definitions of these solutions. Kraus and Parker[4] have shown that although the alternative definitions of the 1 N solution are mutually consistent, the alternative definitions of the 0.1 N and of the 0.01 N solutions are not mutually consistent. Parker and Parker[5] have redetermined the absolute values of the conductance of the Kohlrausch solutions with substantially different results. They proposed new definitions of three different standard solutions, which they call 1, 0.1 and 0.01 demal and gave the results of measurements of the absolute conductance of these solutions. The experimental method used by Parker and Parker was in principle similar to that used by Kohlrausch although evidently improved in many details.

The Editors of the "International Critical Tables" accepted Parker and Parker's work as more reliable than that of Kohlrausch, Holborn and Diesselhorst and have applied corrections to the data in the literature based on the Kohlrausch standards to make them conform to the newer standards of Parker and Parker. As a result very few of the figures for the conductance of solutions found in the "International Critical Tables" agree with the original literature.

In the fifth paper of this series Jones and Bradshaw have described a new and more precise method of making absolute measurements and have redetermined the specific conductance of the three solutions defined by Parker and Parker at 0, 18 and 25°. These results indicate that on the whole the results obtained by Parker and Parker are not as accurate as the earlier work of Kohlrausch, Holborn and Diesselhorst, and that the corrections recommended by Parker and Parker and used by the "International Critical Tables" are unreliable. We have, therefore, undertaken to redetermine the absolute specific conductivity of three standard potassium chloride solutions used by Kohlrausch at 0, 18, 20 and 25° by the new method developed by Jones and Bradshaw. It is hoped that the re-

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[1] Original manuscript received August 3, 1936.

[2] Earlier papers in this series: Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928); Grinnell Jones and G. M. Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411, 1207 (1931); Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933); Grinnell Jones and S. M. Christian, *ibid.*, **57**, 272 (1935); Grinnell Jones and D. M. Bollinger, *ibid.*, **57**, 280 (1935).

[3] F. Kohlrausch, L. Holborn and H. Diesselhorst, *Wied. Ann. Physik*, **64**, 417 (1898).

[4] C. A. Kraus and H. C. Parker, THIS JOURNAL, **44**, 2422 (1922).

[5] H. C. Parker and E. W. Parker, *ibid.*, **46**, 312 (1924).

sults will be helpful in reconciling the great mass of data already in the literature which is based on Kohlrausch's standards with data based on the new standards of Jones and Bradshaw.

The Definitions of the Kohlrausch Standard Solutions.—The book "Das Leitvermögen der Elektrolyte" by Kohlrausch and Holborn, published in 1898, which has probably been used by chemists more than the original article, gives the following definitions (page 76): "Normal Potassium Chloride Solution, that is 74.59 grams of KCl in 1 liter of solution at 18°. Specific gravity at 18°, 1.04492. $\kappa_{18} = 0.09822$. 74.555 grams of KCl, weighed in air, are made up to 1 liter of solution at 18° (for ±1° in temperature the volume is to be taken as ±0.3 ccm. greater), or also 71.422 grams of KCl to 1000 grams of solution, weighed in air, or 76.727 grams in one liter of water at 18°. . . ."

The actual procedure used in the preparation of the solutions which were measured is shown by a study of the original paper which says[3] (p. 435) "Normal Potassium Chloride Solution. For this purpose three varieties of salt were used of which always 74.555 grams were weighed in air and dissolved at 18° to one liter . . . . The determination of the specific gravity gave the value 1.04482 at 18.31° or 1.04492 at 18°." The conductance was measured at 0, 9, 18, 27 and 36° and the values for each 1° interval were obtained by interpolation. The specific conductivity at 18° is given as 0.09822.

The advantages of defining standard solutions in terms of grams of potassium chloride per 1000 g. of solution with both weights corrected to vacuum are discussed in the paper of Jones and Bradshaw and therefore the argument will not be repeated. In order to reproduce Kohlrausch's 1 *N* solution we shall have to assume that the density of the air in his Laboratory was 0.0012 g./ml. and that he used brass weights. On these assumptions the vacuum correction for potassium chloride ($d = 1.987$) is +0.000461 and 74.555 g. in air is equivalent to 74.5894 g. in vacuum. Kohlrausch states that the specific gravity of his normal solution at 18° is 1.04492, but does not state definitely whether this figure is for d^{18}_4 or d^{18}_{18}. However, we have verified this figure experimentally for d^{18}_4 and therefore conclude that Kohlrausch must have meant d^{18}_4 1.04492. Therefore, one kilogram of Kohlrausch's normal solution must have contained 74.5894/1.04492 = 71.3828 g. of potassium chloride per kilogram of solution (both weights corrected to vacuum).

The second alternative definition given in Kohlrausch and Holborn's book is 71.422 g. of potassium chloride in 1000 g. of solution (both weighed in air). Applying the vacuum corrections on the assumption stated above this is equivalent to 71.4549 g. in 1.001006 kg. of solution or 71.3831 g. of potassium chloride per kilogram of solution in vacuum. This agrees with the first definition within four parts per million. Since Kohlrausch only used five significant figures in his definition these two definitions are consistent. Most later experimenters have probably used this definition.

The third alternative definition of the 1 *N* solution in the book is 76.727 g. (air weight) dissolved in 1 liter of water at 18°. Applying vacuum corrections to the salt and taking 1 liter of water at 18° as 998.623 g. (vac.) this definition is equivalent to 71.3813 g. of potassium chloride per kilogram of solution. This is about 0.002% less than the first definition. These three definitions agree within the degree of precision with which the conductivity is given and therefore may be regarded as mutually consistent.

Turning now to the 0.1 *N* solution we find discrepancies between the alternative definitions as has been pointed out by Kraus and Parker. The book (p. 77) says "Tenth Normal Potassium Chloride Solution. One dissolves 7.455 grams, weighed in air, to 1 liter, or 7.430 grams to 1000 grams of solution. Or one dilutes 100 ccm. normal solution to 1000 ccm. This gives $\kappa_{18} = 0.01119$." Here again the original paper (p. 436) reveals the actual method of preparation in the statement "Diluted Potassium Chloride Solutions. The solutions of concentration 1/10, 1/50 and 1/100 were in general prepared from the normal solutions by dilution by volume." The solutions actually measured were evidently prepared by the third alternative method given in the book. Since Kohlrausch does not describe his volumetric procedure in any detail, there is no advantage in attempting to duplicate it experimentally, but we shall have to assume that it was correct and compute the equivalent gravimetric definitions. Since the 1 *N* solution contained 74.5894 g. per liter the 0.1 *N* solution obtained by volumetric dilution should have contained 7.45894 g. per liter at 18°. Kohlrausch does not give the density of this solution but Kraus and Parker give d^{18}_4 1.00343 and we have also verified this figure experimentally. Therefore Kohlrausch's 0.1 N solution must have contained 7.45894/1.00343 = 7.43344 g. of potassium chloride per kilogram of solution (both in vacuum).

The other methods given in the book are not equivalent. 7.455 Grams in air is 7.45844 g. in vacuum which if dissolved in 1 liter of 1.00343 kg. gives 7.43294 g. per kilogram of solution (vac.). 7.430 Grams per kilogram of solution in air is equivalent, after applying the vacuum correction, to 7.43343 g. dissolved in 1.001053 kg. or 7.42561 g. dissolved in 1 kg. of solution. This definition is in error by 0.1%.

The book says (p. 77) "Fiftieth and Hundredth Normal Potassium Chloride Solution. The weighing out of 1.4860 or 0.7430 grams becomes inconvenient. Dilution according to the ratio by volume 1:50 or 1:100 from normal or 1:5 or 1:10 from tenth normal solution is the usual way. κ_{18} = 0.002397 or 0.001225."

Kohlrausch does not give the density of his hundredth normal solution but Kraus and Parker give d_4^{18} 0.99911 and we have verified this figure. A hundredth normal solution prepared by dilution of the normal solution would contain 0.745894 g. (vac.) in 999.11 g. or 0.746558 g. of potassium chloride per kilogram of solution both corrected to vacuum. The alternative definition of 0.7430 g. per kilogram in air is equivalent to 0.742557 g. per kilogram in vacuum. This definition is therefore in error by 0.54% as has already been pointed out by Kraus and Parker.

Experimental

The experimental technique need not be described in detail since it resembled very closely that used by Jones and Bradshaw with some minor improvements suggested by the earlier experience. The chief innovation was that the measurements were carried out at 20° in addition to 0, 18 and 25°, as in the earlier work. In order to avoid any question as to error due to the "Wenner Effect" as discussed in the earlier paper, the entire process of determining the cell constants by the use of mercury as a primary standard was carried through from the beginning with a cell designed so as to avoid error from this cause. Since the earlier experience showed that the cell constants of the Wenner type of cell could be determined by the use of mercury with greater precision than the other parts of the work only one primary cell was used. Most of the other cells were made from the old cells but the cell constants were altered slightly by sealing on new standard-taper ground joints to the filling tubes or new electrode tubes at the ends which made it necessary to anneal the entire cell and remove and replace the platinization. The new platinization was lighter than the old. The differences between the cell constants reported in the two papers should therefore not be interpreted as showing that either the old or new figures are in error.

The data are presented in a different form than was used in the earlier paper, which it is hoped will not only save space in printing but will more readily permit a judgment as to the precision of the data. For this purpose instead of giving the data in full we give the maximum deviation of any measurement of a series from the mean and the "probable error" of the mean, computed by the customary rules given in any book on the theory of errors. It is, of course, well known that these rules assume that the number of determinations is great enough so that the laws of probability may be used and that only accidental unsystematic errors which are as apt to be plus as minus remain. Since systematic errors can never be avoided completely, the "probable error" tends to suggest an overoptimistic judgment as to the precision of the data. We were, of course, acutely aware that the real precision of the data would depend mainly on the success in avoiding systematic errors. The earlier papers in this series explain in some detail the procedures and precautions in our technique which have a claim to novelty. We have endeavored to avoid neglecting other possible sources of systematic error, such as a shift in the ice point of thermometers, but must refrain from a detailed description of such routine matters since their general character is well known.

A very important matter of routine is to make all measurements of resistance with at least two frequencies, since many electrical sources of error which might otherwise be overlooked may be detected in this manner. By measuring each solution in two cells which differ substantially in cell constant, systematic errors in the calibration of the resistance boxes would be revealed if they were appreciable.

Table I gives the results for the cell constant of the primary cell, Z_7, obtained by measurements on the Kelvin bridge when filled with mercury at 0° against two different standard one-ohm coils designated as H and J, each with its Bureau of Standards certificate. As will be seen the two coils give essentially identical results.

TABLE I

CELL CONSTANT OF PRIMARY CELL AT 0°C.

Cell	Based on	Cell constant	Probable error	No. of meas.	Av. dev. from mean
Z_7	Coil H	10584.02	±0.016	5	0.06
Z_7	Coil J	10584.00	± .011	5	.04
Z_7	Accepted av.	10584.01	± .01		

Table II gives the values for the cell constant ratios determined with an alternating current bridge of the new type built by the Leeds and Northrup Company[6] in accordance with the

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(6) P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

principles of design developed by Jones and Josephs. It was calibrated against standard coils having Bureau of Standards certificates. These ratios were determined in an oil thermostat at either 18 or 25°, or both.

Table II

Cell Constant Ratios

	Cell constant ratio	Probable error × 10^6	No. of measurements	Av. dev. from mean × 10^6
Y_3/Z_7	0.1080923	±0.5	8	1.4
Y_4/Z_7	.1043611	±1.1	8	3.6
N_4/Y_3	.0818695	±0.3	17	1.7
N_4/Y_4	.0847953	± .4	17	1.9
N_5/Y_3	.1371218	± .8	17	3.8
N_5/Y_4	.1420222	± .9	17	4.7
Q_3/N_4	.1247929	±1.1	8	4.1
Q_3/N_5	.0745097	±0.6	8	2.0
Q_4/N_4	.1219319	±1.3	8	4.5
Q_4/N_5	.0728015	±0.5	8	1.9

Table III gives the values of the cell constants of the secondary cells and their probable errors, which include both the influence of the error in the ratios and in the cell constants of the larger cell. The change in the cell constant with temperature is computed from the known coefficient of expansion of the glass, 8.08 × 10^{-6} per degree.

Table III

Cell Constants of Secondary Cells

Cell	Based on cell	Temp., °C.	Cell constant	Probable error
Y_3	Z_7	0	1144.050	±0.006
		18	1143.884	± .006
		20	1143.865	± .006
		25	1143.819	± .006
Y_4	Z_7	0	1104.559	± .012
		18	1104.399	± .012
		20	1104.380	± .012
		25	1104.336	± .012
N_4	Y_3	0	93.6628	± .0006
N_4	Y_4	0	93.6615	± .0011
N_4	Av.	0	93.6625	± .0005
		18	93.6489	± .0005
		20	93.6473	± .0005
		25	93.6436	± .0005
N_5	Y_3	0	156.8742	± .0012
N_5	Y_4	0	156.8720	± .0020
	Av.	0	156.8736	± .0010
		18	156.8501	± .0010
		20	156.8481	± .0010
		25	156.8419	± .0010
Q_3	N_4	0	11.68841	± .00012
Q_3	N_5	0	11.68860	± .00011
	Av.	0	11.68851	± .00008
		18	11.68682	± .00008
		20	11.68662	± .00008
		25	11.68615	± .00008
Q_4	N_4	0	11.42045	± .00014
Q_4	N_5	0	11.42063	± .00011
	Av.	0	11.42056	± .00009
		18	11.41890	± .00009
		20	11.41871	± .00009
		25	11.41825	± .00009

Tables IV, V and VI give the specific conductance, κ, (in ohm^{-1} cm.$^{-1}$) of the three standard solutions at 0, 18, 20 and 25° as obtained from each of the cells together with the average deviation of the separate measurements from the mean, and the "probable error" of the mean. In the work on 1 and 0.1 N solutions the measurements at 18 and 25° were usually made in succession without removing the solution from the cells. A different series of solutions were used for the measurements at 20 and 0°, which were also made in succession without removing the solutions from the cells. With the 0.01 N solutions the procedure was different in that the measurements were made at 18, 20 and 25° without removing the solutions from the cells and an independent series of solutions was used for the measurements at 0°. The measured specific conductivity has been corrected in each case for the conductivity of the water used, amounting to about 1.1 × 10^{-6} at 25°. The "probable error" of the mean is computed from the deviations of the individual measurements and the probable error of the cell constant, but any errors in the temperature scale will not be reflected in the computed probable error since such errors are systematic. The thermometers used were the same as in the previous work and have been described in the previous paper. Although these thermometers were of exceptionally good quality, it seems probable that the greatest systematic errors in the final results may be in the temperature scale. The data are possibly less reliable at 0° than at the other temperatures because of the difficulty in maintaining this temperature inside of an oil-bath. The method of maintaining the cells at 0° by packing them inside a solid block of paraffin formerly used was abandoned in favor of immersion in a liquid paraffin oil in a metal container which was completely immersed in ice. This oil cannot be stirred without causing overheating because the heat generated thereby cannot be dissipated rapidly enough. A thermometer cannot be inserted into the oil because the heat conductivity of the thermometer itself would maintain the temperature above 0°. It is necessary to be patient until the resistance readings become independent of time. The maximum resistance obtainable was accepted. On the other hand, at the higher temperatures the thermostat can be stirred with advantage because the thermostat contained a cooling coil with cold water circulating in it and the automatic adjustment of the heat balance takes care of the heat generated by stirring.

TABLE IV

SPECIFIC CONDUCTANCE × 10^6 OF 1 NORMAL POTASSIUM CHLORIDE SOLUTIONS

Kohlrausch's 1 *N* KCl containing 71.3828 g. of potassium chloride per 1000 g. of solution, both weights corrected for air buoyancy and the specific conductance corrected for the conductance of the water used.

Temp., °C.	Cell	$\kappa \times 10^6$	Probable error × 10^6	No. of solns.	Av. dev. from mean × 10^6
0	Y_3	65432.3	±1.3	8	4.3
0	Y_4	65428.2	±1.4	8	3.5
0	Av.	6543_0	±1.0		
18	Y_3	98201.1	±1.1	7	2.8
18	Y_4	98200.3	±1.4	7	2.9
18	Av.	9820	±0.9		
20	Y_3	102025.5	± .9	8	2.3
20	Y_4	102021.7	±1.3	7	2.1
20	Av.	10202_4	±0.7		
25	Y_3	111733.8	±1.3	7	3.7
25	Y_4	111731.2	±1.9	7	4.6
25	Av.	11173_3	±1.1		

TABLE V

SPECIFIC CONDUCTANCE × 10^6 OF 0.1 NORMAL POTASSIUM CHLORIDE SOLUTIONS

Kohlrausch's 0.1 *N* KCl containing 7.43344 g. of potassium chloride per 1000 g. of solution, both weights corrected for air buoyancy and the specific conductance corrected for the conductance of the water used.

Temp., °C.	Cell	$\kappa \times 10^6$	Probable error × 10^6	No. of solns.	Av. dev. from mean × 10^6
0	N_4	7154.26	±0.08	7	0.19
0	N_5	7154.32	± .23	8	.73
0	Av.	$7154.3_{}$	± .08		
18	N_4	11191.88	± .14	8	.42
18	N_5	11191.99	± .20	8	.57
18	Av.	$11191._9$	± .11		
20	N_4	11667.65	± .09	6	.16
20	N_5	11667.52	± .13	6	.30
20	Av.	$11667._6$	± .07		
25	N_4	12886.04	± .16	8	.43
25	N_5	12886.30	± .12	8	.28
25	Av.	$12886._2$	± .10		

Although the experience gained in the earlier similar investigation in this Laboratory was very helpful and much of the same apparatus was used, nevertheless the actual experimental data are entirely independent of any measurements made by Dr. Bradshaw. Everything which could influence the numerical results, such as the calibration of the weights and resistance coils and the ice points of the thermometers, was checked independently.

TABLE VI

SPECIFIC CONDUCTANCE × 10^6 OF 0.01 NORMAL POTASSIUM CHLORIDE SOLUTIONS

Kohlrausch's 0.01 *N* KCl containing 0.746558 g. of potassium chloride per 1000 g. of solution, both weights corrected for air buoyancy and the specific conductance corrected for the conductance of the water used.

Temp., °C.	Cell	$\kappa \times 10^6$	Probable error × 10^6	No. of solns.	Av. dev. from mean × 10^6
0	Q_3	775.144	±0.015	6	0.04
0	Q_4	775.114	± .009	6	.02
0	Av.	775.1_2	± .008		
18	Q_3	1222.721	± .020	8	.06
18	Q_4	1222.641	± .025	8	.08
18	Av.	1222.6_9	± .016		
20	Q_3	1275.770	± .027	8	.09
20	Q_4	1275.680	± .026	8	.09
20	Av.	1275.7_2	± .02		
25	Q_3	1411.479	± .023	8	.07
25	Q_4	1411.406	± .027	8	.08
25	Av.	1411.4_5	± .02		

Table VII summarizes the results and compares the corrections recommended by Parker and Parker and used by the "International Critical Tables" for a systematic recalculation of the data in the literature with the corrections computed from our measurements. As will be seen our results do not confirm the reliability of the corrections recommended by Parker and Parker. In only one of the nine cases is our correction within 0.03% of that recommended by Parker and Parker. In six of the nine cases our results agree with Kohlrausch better than they do with Parker and Parker and in four of the nine cases we even differ as to the sign of the correction which should be applied to Kohlrausch's values. In attempting to apply corrections to the data in the literature due consideration must be given to the possibility of confusion caused by the alternative definitions given in the book, "Das Leitvermögen der Elektrolyte." Many authors do not make it clear which one of the alternative definitions they actually used.

Our new measurements make it probable that on the whole the accuracy of the data on the conductance of solutions given in the "International Critical Tables" has not been improved by the recalculation by the use of Parker and

TABLE VII

CORRECTIONS TO BE APPLIED TO CONDUCTANCE DATA BASED ON KOHLRAUSCH STANDARD POTASSIUM CHLORIDE SOLUTIONS

	0°	18°	20°	25°
1 *N* KCl 71.3828 g. KCl per 1000 g. of solution in vacuum				
Kohlrausch	0.06541	0.09822	0.10207	0.11180
Parker's values	.065312	.098116		.111687
Parker's corrections, %	− .150	− .108		− .101
Our new values	.065430	.098201	.102024	.111733
Recommended corrections, %	+ .031	− .019	− .045	− .060
0.1 *N* KCl 7.43344 g. KCl per 100 g. solution in vacuum				
Kohlrausch	0.00715	0.01119	0.01167	0.01288
Parker's values	.0071416	.0111846		.0128765
Parker's corrections, %	− .118	− .048		− .027
Our new values	.0071543	.0111919	.0116676	.0128862
Recommended corrections, %	+ .060	+ .017	− .021	+ .048
0.01 *N* KCl 0.746558 g. KCl per 1000 g. solution in vacuum				
Kohlrausch	0.000776	0.001225	0.001278	0.001413
Parker's values	.00077422	.00122238		.00141037
Parker's corrections, %	− .229	− .214		− .186
Our new values	.00077512	.00122269	.00127572	.00141145
Recommended corrections, %	− .114	− .189	− .179	− .110

Parker's standards instead of the Kohlrausch standards originally used by most experimenters.

Summary

1. The absolute specific conductances of the 1, 0.1 and 0.01 *N* potassium chloride solutions recommended by Kohlrausch as a standard of reference for conductivity measurements have been redetermined.

2. The results indicate that the corrections used by the "International Critical Tables" in the recalculation of the conductance data are unreliable.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Kinetics of Activated Sorption of Hydrogen on Chromic Oxide Gel[1]

BY LOYAL CLARKE,[2] L. S. KASSEL[3] AND H. H. STORCH[4]

Introduction

Burwell and Taylor[5] have recently presented more than usually complete data on the kinetics of activated sorption of hydrogen on a chromium oxide catalyst as a function of pressure and temperature. The present paper derives from their data an empirical relationship which is satisfactory, except for small and for very large sorption. The form of this relation suggests a model of the sorption process, which permits derivation of the equation for moderate sorptions, and accounts at least qualitatively for its failure at extreme conditions.

When the amount of hydrogen sorbed computed by Burwell and Taylor is plotted against time and a smooth curve drawn through the points, it was found that extrapolation to the starting time would, taken naïvely, indicate an appreciable amount of sorption coincident with the beginning of the experiment. The results of these extrapolations are given in Table I. It will be seen that for all the experiments at 1 atmosphere this initial amount is about 1.3 cc., at one-half atmosphere about 0.8, and at a quarter atmos-

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[5] R. L. Burwell, Jr., and H. S. Taylor, THIS JOURNAL, **58**, 697–705 (1936).

TABLE I

EXTRAPOLATION OF SORPTION DATA TO STARTING TIME

Temp., °K.	383.5	405	427	457	491	457
Catalyst	9	9	9	9	9	10
Extrapolation in cc. when pressure is:						
1 atmosphere	1.34	1.42	1.26	1.30	1.20	1.21
$^1/_2$ atmosphere	0.76	0.86	0.80	0.80	0.80	0.96
$^1/_4$ atmosphere	.57	.50	.43	.50	.50	.43
$^1/_8$ atmosphere						.15

phere 0.5, or approximately $0.2 + 1.1\,p$. It is quite possible that the dead-space determination using helium is not the correct dead space available for hydrogen,[6] but regardless of cause it is believed that a large fraction of these initial amounts represents a phenomenon other than the slow sorption process.[7] Accordingly the amounts sorbed, as given by Burwell and Taylor, have been corrected by subtraction of the extrapolations given in Table I. The corrected figures appear to approximate the true amount of activated sorption. This is indicated by the improved correlations obtained by means of the revised data.

Burwell and Taylor observed that the data of the separate experiments would approximate a common curve when the amount of sorption, S, is plotted against bt, where b is a constant whose relative value is characteristic of the pressure and the temperature. This relation is, as Burwell and Taylor themselves state, only approximate, but it is improved somewhat by the use of our revised values instead of the uncorrected data. The representation of b by the equation $b = p^nAe^{-Q/RT}$ suggested by Burwell and Taylor is also improved but still inadequate, since the best values of n computed at 383.5, 405, 427, 457, and 491°K. were, respectively: 1.00, 1.00, 0.84, 0.74, and 0.60. Values of Q in the temperature range of 405 to 491°K. as graphically computed from mean values of $p^{0.8}t$ at sorptions of 1, 2, 3, 4, 5 and 6 cc. were, respectively: 15.3, 18.3, 19.0, 19.2, 19.7 and 21.0 kcal. Little impart may be attached to the 1 cc. value and the trend in the other values is comparable with the accuracy of computation and would not be serious were it not that the fluctuation of n impairs the utility of the relation and obscures the interpretation of Q as an activation energy.

Kinetic Model

The existence of a pressure effect definitely less than first order seems to force the assumption that the initial sorption process is followed by some more or less slow rearrangement. We propose to investigate the consequences of this assumption in a relatively simple form. It will be supposed that the sorbent contains n primary adsorption centers and N secondary centers, only the former of which are capable of capturing gas molecules. The secondary centers can take molecules from, and give molecules to, the primary centers but have no kinetic relations with the gas. The fraction of primary centers covered is Θ, that of secondary centers is α, and the gas pressure is p. The rates of the various allowed transfers, in molecules per secondary are then taken to be as

gas ⟶ primary centers $npk_1\,(1 - \Theta)$
primary ⟶ secondary centers $nNk_2\Theta\,(1 - \alpha)/(1 + R\alpha)$
secondary ⟶ primary centers $nNk_3\alpha\,(1 - \Theta)/(1 + R\alpha)$
primary centers ⟶ gas $nk_4\Theta$

The significance of the factor $1 + R\alpha$ will be discussed later in the paper. The controlling differential equations are then

$$\mathrm{d}N\alpha/\mathrm{d}t = nN[k_2\Theta\,(1 - \alpha) - k_3\alpha\,(1 - \Theta)]/(1 + R\alpha)$$
$$\mathrm{d}(n\Theta + N\alpha)/\mathrm{d}t = n[pk_1\,(1 - \Theta) - k_4\Theta]$$

If n and N are of the same order of magnitude we proceed as follows:

(1) Define a new variable β, proportional to the total adsorption, by the relation

$$n\Theta + N\alpha = n\beta$$

and use this relation to eliminate α from the differential equations.

(2) Introduce for Θ the power series expansion

$$\Theta = \beta + u_2\beta^2 + u_3\beta^3 + \ldots$$

obtaining two differential equations of the form

$$\mathrm{d}\beta/\mathrm{d}t = f\,(\beta)$$

(3) Expand the two right-hand members and determine the parameters u_i by equating coefficients of like powers of β.

(4) Solve the resulting single differential equation for t as a power series in β.

The result is

$$t = \beta/pk_1 + (1/pk_1 + k_4/p^2k_1^2)(\beta^2/2) + \ldots$$

The coefficients of β and β^2 do not have the form of pressure dependence necessary to give an

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(6) *Cf.* experiments reported by Benton at Pittsburgh meeting of American Chemical Society, September 7-12, 1936.

(7) Burwell and Taylor also suggested that a certain amount of the hydrogen loss was due to causes other than the one of interest and treated their data both with and without appropriate corrections therefore. We found difficulty in understanding the method of deduction of these values and have chosen the above method because it is direct, independently reproducible, and reasonably free from predisposition toward any particular relationship connecting the data at various pressures and temperatures.

apparent order less than unity and this model is thus unsatisfactory. The secondary centers, in fact, do not enter into these coefficients at all; k_2 first appears in the coefficients of β^3, and k_3 in that of β^4.

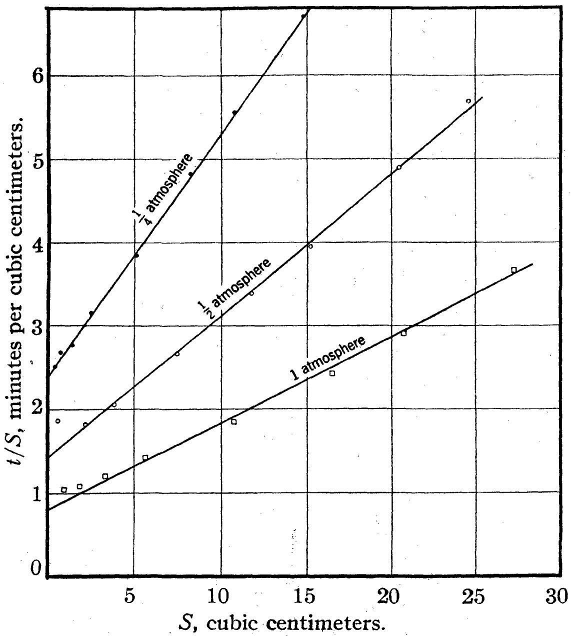

Fig. 1.—Sorption data at 457°K.

If n is very small compared to N, which is certainly a plausible condition, the foregoing analysis remains perfectly correct, but is no longer useful. Moderate values for β, such that terms beyond β^2 may be discarded, correspond to extremely small values of the total absorption, quite outside the range of measurement. A more appropriate solution for this case is obtained by a method similar to that used for chain reactions. Since, beyond the very earliest stages of the reaction, $n\Theta \ll N\alpha$, it follows that $dn\Theta/dt \ll dN\alpha/dt$. We may therefore use

$$dn\Theta/dt = 0$$

to determine a steady state value of Θ as a function of α. This functional relation is used to eliminate Θ, giving a differential equation of the form $d\alpha/dt = f(\alpha)$ which has as a solution the power series expansion

$$\begin{aligned} nt = {} & [1/k_2 + (N/k_1 + k_4/k_1k_2)(1/p)]\alpha \\ & + (1/2)\{((R + 1)/k_2 + [(R + 1)k_4/k_1k_2 + Nk_3/k_1k_2 \\ & + k_3k_4/k_1k_2^2)](1/p) \\ & + (Nk_3k_4/k_1^2k_2 + k_3k_4^2/k_1^2k_2^2)(1/p^2)\}\alpha^2 + \ldots \end{aligned}$$

When $k_4 \ll k_1p$, which is true at pressures where the equilibrium adsorption is large, the terms in $(1/p^2)$ make a negligible contribution to the coefficient of α^2.

Using the assumptions $k_4 \ll k_2N$ and $k_4 \ll k_1p$, both of which are probably justified, we obtain

$$nt = (1/k_2 + N/k_1p)\alpha + 1/2[(R + 1)/k_2 + Nk_3/k_1k_2p]\alpha^2$$

Application to Data of Burwell and Taylor

$N\alpha$ is obviously the amount of sorption and is conveniently designated by a single letter S. We make the further substitutions

$$\frac{1}{nk_1} = B_1,\ \frac{1}{nKk_2} = B_2,\ \frac{k_3}{2nNk_1k_2} = C_1,\ \frac{R + 1}{2nN^2k_2} = C_2$$

and obtain

$$pt = (B_1 + B_2p)S + (C_1 + C_2p)S^2$$

The experiments of Burwell and Taylor were performed at constant pressures so that the coefficients of S and S^2 should be constant for any single experiment.

A plot of t/S against S should therefore be a straight line. Burwell and Taylor's data (corrected as described) for catalyst 9 at 457°K. are so plotted in Fig. 1. The relation is adequate for values of adsorption between 2.5 and 25 cc. The B_2 and C_2 terms are relatively unimportant at 383.5 and 405°K., so that the data for different pressures fall on a comparatively straight line when pt/S is plotted against S as in Fig. 2.

The best values of these constants are given in Table II under the heading "experimental."

Returning to the significance of these constants in the kinetic derivation

$$\begin{aligned} k_1 &= 1/nB_1 \\ k_2 &= 1/nNB_2 \\ k_3 &= 2C_1/nB_1B_2 \\ R + 1 &= 2NC_2/B_2 \end{aligned}$$

TABLE II

BEST VALUES OF CONSTANTS IN THE EQUATION $pt = (B_1 + B_2p)S + (C_1 + C_2p)S^2$. UNITS p IN ATM., t IN MINUTES, S IN CC.

	B_1		B_2		C_1		C_2	
T, °K.	Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.
383.5	1.2	23.5	0	11.5	11.6	12.4	0	0.92
405	2.9	6.67	0	3.80	3.14	2.31	0	.30
427	2.05	2.09	1.275	1.38	0.44	0.47	0.11	.11
457	0.49	0.47	0.43	0.41	.064	.063	.033	.033
491	.112	.122	.125	.123	.0101	.0103	.0095	.0098

The "theoretical" values of the constants given in Table II are computed from the equations

$$\log \frac{B_1}{\sqrt{T}} = \frac{4110}{T} - 10.63$$

$$\log B_2 = \frac{3450}{T} - 7.94$$

$$\log \frac{C_1}{B_1 B_2} = -\frac{2060}{T} + 4.03$$

$$C_2/B_2 = 0.08$$

The values for the lower temperatures are in disagreement with these equations; however, the total amount of sorption at these temperatures is small and, in fact, of the order for which the relation fails at higher temperatures. This failure is consistent with the theoretical analysis made above. Furthermore, this is not unexpected since the subtractive corrections as determined by the experimental intercepts are of the same order of magnitude as the total sorption at the lower temperatures.[8] The relation $pt = (B_1 + B_2p)S + (C_1 + C_2p)S^2$ is therefore of a semi-empirical nature when used in experiments involving very small sorptions.

The theoretical value of the ratio C_2/B_2 is $(R + 1)/2N$. The experimental value is approximately 0.08, and hence $\alpha = 0.16\ S/(R + 1)$. If $R = 0$, $\alpha = 1$ would correspond to $S = 6.25$ cc., whereas actually the saturation absorption is probably 100 cc. or more. The value of R needed to agree with these data is therefore at least 15. This necessary correction factor, $(1 + R\alpha)^{-1}$, may be interpreted as representing a reduced rate of transfer between primary centers and non-adjacent secondary centers; its form, however, is determined by mathematical convenience rather than physical considerations.

The experimental results for the highest three temperatures then give for k_1 an activation energy of 18.75 kcal., for k_2, 15.75 kcal. and for k_3, 9.4 kcal. The relative activation energies for k_2 and k_3 indicate a heat of adsorption for the primary centers 6.3 kcal. greater than for the secondary centers. This difference is consistent with the greater activity of the primary centers in adsorbing gas molecules. If the rate of adsorption on the primary centers is equal to the rate of collision of gas molecules $Xe^{-19,000/RT}$, the area of these centers must be 1600 sq. cm. They would then have an adsorptive capacity of the order of 0.5 cc. This value is sufficiently small to justify the assumption $n \ll N$. It is, at the same time, large enough to make this assumption slightly erroneous, and thus perhaps to account for the observed systematic distortions in the experimental curves for adsorptions less than 2.5 cc.

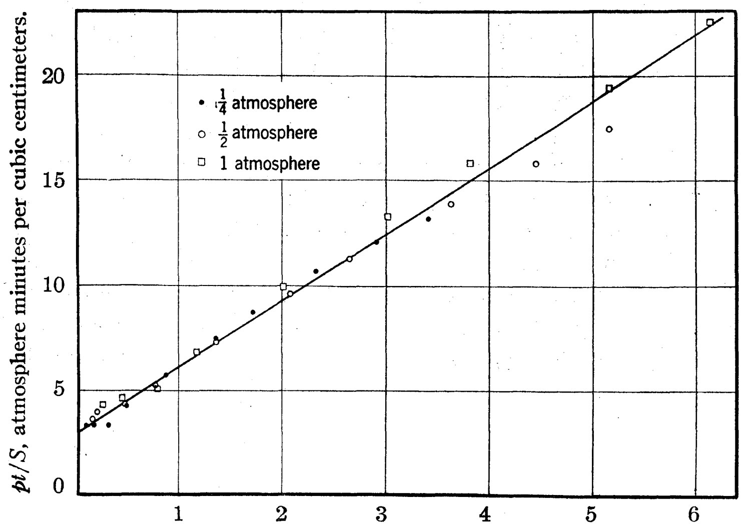

Fig. 2.—Sorption data at 405°K.

Discussion

The failure of results at the lowest temperatures to agree with extrapolated constants is quite possibly associated with the great importance of the amount of primary adsorption for the

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(8) The method used in adjusting the data implicitly assumes that the activated sorption of hydrogen on secondary centers is the only process resulting in an appreciable withdrawal of hydrogen after the first few minutes. Burwell and Taylor have suggested that some of the sorption occurring after several minutes also represents phenomena other than that of interest and should be included in the subtractive corrections. It has been found possible to secure excellent agreement between equations obtained by the use of the theoretical constants given in Table II and the data for the latter portion of the runs at 383.5°K. (after forty minutes) and 405°K. (after twenty minutes) by subtraction from the original data of the following constants:

p, atm.	383.5°K.	405°K.
1	2.25 cc.	2.08 cc.
0.5		1.38
.25	1.30	0.85

The difference between these values and our previous corrections may represent either primary sorption or an entirely unrelated process, or both. This suggests the adoption of a more refined method of determining the corrections. This could be done by fitting the original data to equations of form: $t = a + bS + cS^2$ and computing the subtractive corrections and the other constants therefrom. The foregoing analysis would be used only for rejection of points outside of the expected range of validity. Such a revision has not been undertaken however, because the high temperature experiments would still have to carry the burden of the proof and their interpretation would not be materially altered.

small sorptions to which data at these temperatures are limited.[8] It does not appear possible to decide definitely whether this type of analysis is applicable to the lower temperatures without extensions of the data to larger sorptions. For the higher-temperature region, however, there seems little doubt that the model yields a satisfactory interpretation of the experimental data. It does not follow that the underlying assumptions are entirely correct. As has already been suggested, the correction factor $(1 + R\alpha)^{-1}$ is introduced in an arbitrary way.

A precise treatment of the diffusion factor would necessitate a consideration of the geometry of the model. Such an analysis might conceivably result in a decision as to whether the phenomenon of slow sorption on chromic oxide gel corresponds more closely to a surface diffusion from active centers,[9] to surface adsorption followed by diffusion to the interior,[10] or to diffusion into Smekal cracks.[11] The assumption that there is no direct sorption on the secondary centers can represent at best merely an approximation to the case where the amount of such sorption is small. The sorptive regions of a real catalyst may not be amenable to a classification as simple as that which we have used, and although the introduction of more types of centers would probably lead to equations of the same form as we have found, the experimental constants would be less simply related to the fundamental rate constants. The model makes no assumption with regard to the physical nature of the sorption centers, and its success therefore contributes nothing to the solution of this problem.

Summary

An analysis of Burwell and Taylor's data on the activated sorption of hydrogen by chromium oxide has led to the derivation of a rate equation that fits the data for moderate amounts of sorption very well. The derivation is based on a simple model of the sorption process, involving primary adsorption followed by diffusion to secondary centers. This model also accounts, qualitatively at least, for the failure of the equation at extreme conditions.

PITTSBURGH, PA. RECEIVED DECEMBER 30, 1936

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[9] H. S. Taylor, *Z. Elektrochem.*, **35**, 542–549 (1929).

[10] A. F. H. Ward, *Proc. Roy. Soc.* (London), **A133**, 506–535 (1931).

[11] Adolf Smekal, *Z. Elektrochem.*, **35**, 567–573 (1929).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHERN MONTANA COLLEGE]

Acylselenoureas

BY IRWIN B. DOUGLASS

The investigation of the acyl isothiocyanates and certain acylthiourea derivatives by the author[1] and a review of certain organic selenium derivatives by Bradt[2] suggested the possibility that acid chlorides might react with metallic selenocyanates in a manner analogous to their reaction with the thiocyanates.

The work thus far accomplished indicates that there is a vigorous reaction when acid chlorides and KSeCN are brought together in acetone solution. In no case has the product (I) been

$$\mathrm{RCOCl + KSeCN \longrightarrow RCOCSeN\ (I) + KCl} \quad (1)$$

isolated and the evidence thus far accumulated does not definitely establish it as a selenocyanate, an isoselenocyanate, or an equilibrium mixture of the two. The fact, however, that (I) in acetone solution when treated with amines forms selenoureas according to reaction (2) indicates

$$\mathrm{RCOCSeN + R'NH_2 \longrightarrow RCONHCSeNHR'} \quad (2)$$

that (I) must have the structure RCONCSe or at least must consist of an equilibrium mixture containing a large proportion in that form. On the basis of this evidence, the acyl derivatives resulting from the reactions between acid chlorides and potassium selenocyanate will be referred to as acyl isoselenocyanates or acylselenocarbimides.

This paper describes the properties of a few acylselenoureas prepared by reactions (1) and (2). The grouping RCO– was varied to include acetyl, carbethoxy, pyromucyl and benzoyl so as to gain some idea of the behavior of various acyl isoselenocyanates when treated with aniline, and the group R′ was varied to determine the behavior of benzoyl isoselenocyanate when treated with different amines.

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[1] Douglass and Dains, THIS JOURNAL, **56**, 719, 1408 (1934); Douglass and Forman, *ibid.*, **56**, 1609 (1934).

[2] Bradt, *J. Chem. Ed.*, **12**, 363 (1935).

Experimental

Acyl isoselenocyanate solutions were prepared by dissolving slightly more than 0.1 mole of potassium selenocyanate in 200 ml. of acetone and adding to the solution exactly 0.1 mole of acid chloride. In each case an immediate exothermic reaction took place with the separation of potassium chloride and the formation of a colored solution. The solutions were used immediately to react with amines to form selenoureas. No attempts have been made as yet to isolate the acyl isoselenocyanates.

With the addition of the last acid chloride to the selenocyanate solution, 0.1 mole of amine, in acetone solution, was added as rapidly as the vigorous boiling of the reaction mixture would permit. Lower yields of selenourea seemed to be obtained when the addition of amine was delayed. When the reaction had subsided, the mixture was poured slowly with stirring into 600–800 ml. of cold water. The solid selenourea which separated was removed by filtration and crystallized from a suitable solvent.

Potassium selenocyanate was prepared by fusing together potassium cyanide and slightly more than an equivalent amount of black powdered selenium.[3] The black melt was dissolved in water, and the solution boiled to coagulate the undissolved selenium. The solution was then filtered and evaporated with stirring until the temperature of the melted residue had reached 190°. The product was broken up as it cooled, pulverized, and used without further purification.

Constitution of the Selenoureas.—An alcoholic solution of the product resulting from benzoyl chloride, potassium selenocyanate, and aniline was boiled with alcoholic silver nitrate solution. After removing the precipitated silver selenide white needles having a melting point of 209° (corr.) separated from the alcoholic solution. Similar treatment of α-benzoyl-β-phenylthiourea yielded an identical product. A mixed melting point of the two was not lowered. The highest melting point recorded for α-benzoyl-β-phenylurea is 210°.[4]

Anal. Calcd. for $C_{14}H_{12}O_2N_2$: N, 11.67. Found (deselenized product): N, 11.49.

Bitter Taste of Benzoylselenourea.—While working with benzoylselenourea it was noticed that when the crystals were disturbed a very bitter dust arose. Since certain of the thioureas are very bitter to some individuals but have no taste to others,[5] it seemed of interest to determine whether there would be individuals taste-blind to benzoylselenourea. Strips of filter paper, dipped into a dilute alcoholic solution of benzoylselenourea, were cut into small pieces and given to Northern Montana College students to taste. Of 175 cases 131 reported the papers as having a decidedly bitter taste whereas 44 reported either no taste or some taste other than bitter.

Yields.—The percentage yields of the selenoureas varied somewhat with the acid chloride used and also with the amine used. The data in regard to yields can be considered as only of a qualitative nature, however, for there was considerable variation in yield with successive preparations of the same selenourea. It would seem that there are factors affecting yield not yet fully understood. Low yields were usually accompanied by the production of colored by-products.

Acetyl Isoselenocyanate and Aniline.—The reaction of acetyl isoselenocyanate with aniline seems to follow the same two courses as acetyl isothiocyanate and aniline.[6] In the preparation of α-acetyl-β-phenylselenourea a yield of only 12% was obtained. From the water into which the reaction mixture was poured a 27% yield of acetanilide, based on the original quantity of aniline was obtained as a first crop.

Selenoureas

Benzoyl-.—White prisms from alcohol, m. p. 194–195° (corr.), yield 27%. Spontaneously oxidized in alcoholic solutions to selenium and benzoylurea. *Anal.* Calcd. for $C_8H_8ON_2Se$: N, 12.34. Found: N, 12.25.

α-Benzoyl-β-phenyl-.—Long yellow needles from alcohol, m. p. 144–145° (corr.), yield, 72%. A mixed melting point of this compound with the corresponding thiourea was not lowered appreciably. *Anal.* Calcd. for $C_{14}H_{12}ON_2Se$: N, 9.24. Found: N, 9.09.

α-Benzoyl-β-o-tolyl-.—Long yellow prisms from alcohol, m. p. 124–125° (corr.), yield 70%. *Anal.* Calcd. for $C_{15}H_{14}ON_2Se$: N, 8.83. Found: N, 8.99.

α-Benzoyl-β-p-tolyl.—Yellow needles from a mixture of dioxane and alcohol, m. p. 154–155° (corr.), yield 56%. *Anal.* Calcd. for $C_{15}H_{14}ON_2Se$: N, 8.83. Found: N, 8.90.

α-Benzoyl-β,β-naphthyl-.—Yellow prisms from dioxane, m. p. 171–172° (corr.), yield 58%. *Anal.* Calcd. for $C_{18}H_{14}ON_2Se$: N, 7.93. Found: N, 7.86.

α-Benzoyl-β-benzyl-.—Long orange prisms from alcohol, m. p. 115–116° (corr.), yield 19%. *Anal.* Calcd. for $C_{15}H_{14}ON_2Se$: N, 8.83. Found: N, 8.93.

α-Benzoyl-β,β-diethyl-.—Yellow needles and yellow prisms, m. p. 110° (corr.), yield 49%. *Anal.* Calcd. for $C_{12}H_{16}ON_2Se$: N, 9.93. Found: N, 9.76.

α-Acetyl-β-phenyl-.—Pink plates from alcohol, m. p. 184–185° (corr.), yield 12%. *Anal.* Calcd. for $C_9H_{10}ON_2Se$: N, 11.62. Found: N, 11.43.

α-Phenyl-β-pyromucyl-.—Yellow needles from alcohol, m. p. 106–107° (corr.), yield 24%. *Anal.* Calcd. for $C_{12}H_{10}O_2N_2Se$: N, 9.56. Found: N, 9.52.

An attempt was made to prepare α-carbethoxy-β-phenylselenourea, but no solid product was isolated. The reaction between ethyl chlorocarbonate and potassium selenocyanate was smooth and resulted in the formation of practically no colored by-products. Likewise the reaction of the supposed carbethoxy isoselenocyanate with aniline appeared to be normal. The colorless oil which separated when the mixture was poured into water would not solidify, however, and on standing for several days acquired such an offensive odor that it was discarded.

Summary

1. The action of acid chlorides on acetone solutions of potassium selenocyanate yields compounds which react with amines to form selenoureas.

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[3] Obtained through the courtesy of the Anaconda Copper Mining Company.

[4] Billeter *Ber.*, **36**, 3220 (1903).

[5] Fox, *Proc. Nat. Acad. Sci. U. S.*, **18**, 115 (1932).

[6] Dixon and Hawthorne, *J. Chem. Soc.*, **87**, 468 (1905).

2. The compounds formed by the action of acid chlorides on potassium selenocyanate, although not yet isolated, appear to be very similar in their reactivity to the acyl isothiocyanates and are believed to be acyl isoselenocyanates.

3. Benzoylselenourea possesses a very bitter taste to most individuals, but is tasteless to others, thus emphasizing the similarity of the selenoureas to the thioureas.

HAVRE, MONTANA RECEIVED FEBRUARY 18, 1937

[CONTRIBUTION FROM LAND-WHEELWRIGHT LABORATORIES]

Optical Properties and Polymorphism of Paraffins

BY C. D. WEST

When a molten paraffin or similar long chain compound is allowed to solidify in a film on a flat glass surface, the film, in spite of being turbid to the naked eye, and showing many randomly oriented small crystals under the microscope, still has sufficient homogeneity to show a peculiar effect when examined with a total reflection refractometer. Instead of one boundary between total and ordinarily reflected light, two such boundaries of a somewhat diffuse character are observed, separated by an interval of up to 0.05 unit in the refractive index scale. The state of polarization of the light at these boundaries proves that the film is optically equivalent to the basal section of a uniaxial positive crystal.

This effect was first described in a paper by Camerer,[1] then by Gaubert,[2] and by Walter.[3] Vorländer and Selke[4] showed that the effect is to be observed with a great variety of pure long chain compounds (paraffins, unsaturated fatty acids, esters of fatty acids, alcohols and ketones, etc.) which solidify in soft solid crystals.

In the past year Page[5] published measurements on five natural paraffins with melting points in the range 49.4–60.6°. Page assigned an incorrect optical character to his films; he arbitrarily called the ordinary refractive index the extraordinary, and *vice versa*. His calculations based on this error are accordingly incorrect. He carried his measurements for each specimen through a considerable temperature range. The irregularity of these curves at temperatures near the melting points suggests that at least some of his materials (for example, that melting at 60.6°) underwent polymorphic transitions in the course of the measurements, as they would be expected to do according to the X-ray structure work that has been published on this point.

More recently Seyer and Fordyce[6] gave refractive index data for the pure paraffin dicetyl (dotriacontane, $C_{32}H_{66}$) in the solid state from 30° up to the melting point, 70°. These writers failed to note the double edge of total reflection, nor did they take into consideration the fact that this material has a sharp reversible inversion at 5° below its melting point. Rather they concluded from their refractive index curve, together with the solubility curves in propane and butane, that dicetyl has a transition at 55°.

The prior work of Piper and co-workers[7] showed clearly that dicetyl has a sharp reversible transition at about 65°. This was observed macroscopically, microscopically and by means of X-rays. Other straight chain paraffins near to dicetyl all exhibit the same transition about 5° below the melting point.[8]

In the following is described a repetition of the work of Seyer and Fordyce with dicetyl, rather for the purpose of illustration than to give the precise numerical constants of this material in a state of known purity.

Experimental

An Abbe refractometer with front opening for the front or refracting prism (Bausch and Lomb) was used. The dicetyl was obtained from Eastman Kodak Company; it melts sharply at 69.5–69.7°, and solidifies at 68.8–67.7°. For some of the measurements the molten material was poured onto the refracting prism and allowed to solidify without closing the back prism; for others the back prism was closed after melting the material on the front prism. The character and position of the edges is the same in the

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[1] R. Camerer, *Ann. Physik*, **54**, 84–103 (1895).

[2] P. Gaubert, *Bull. soc. franç. mineral.*, **33**, 326 (1910).

[3] R. Walter, *Ber.*, **59**, 971–972 (1926).

[4] D. Vorländer and W. Selke, *Z. physik. Chem.*, **129**, 435–474 (1927).

[5] J. M. Page, Jr., *Ind. Eng. Chem.*, **28**, 856–859 (1936).

[6] W. F. Seyer and R. Fordyce, THIS JOURNAL, **58**, 2029 (1936).

[7] S. H. Piper and others, *Biochem. J.*, **25**, 2027 (1931).

[8] L. Deffet, *Bull. soc. chim. Belg.*, **44**, 97 (1935), reported the melting point 70.0° and the transition point 64.3° for dicetyl at atmospheric pressure.

two cases, but of course the temperature control is better when the prisms are closed and water circulates about both of them.

The character of the edges was identified with a polarizing disk (obtainable from the Polaroid Corporation, Boston, or other dealers) over the ocular. The well-known rule for uniaxial sections or films perpendicular to the optic axis may be stated: When the vibration direction of the polarizer is vertical, *i. e.*, parallel to the plane of incidence, the boundary marking the ordinary index disappears, the sharpness of the extraordinary boundary is enhanced; when the vibration direction of the polarizer is horizontal, *i. e.*, perpendicular to the plane of incidence, the extraordinary boundary disappears, the sharpness of the ordinary boundary is enhanced. If the film under examination is isotropic, the boundary marking its refractive index does not disappear for any azimuth of the polarizer. These statements are true, whether the light is admitted through the front prism (reflection position) or through the back prism (grazing incidence position). A polarizer is indispensable in work with materials that may form anisotropic films, in *finding*, in *identifying*, and in *setting on the cross hairs* the boundaries observed with a total reflection refractometer.

Other materials known to form, under suitable conditions, uniaxial films on flat glass surfaces are liquid crystalline substances, cellulose derivatives, gelatine, agar, etc. I hope to describe some of these films at a later date.

Results

Refractive index measurements of dicetyl, believed to be accurate to better than 0.001 unit, are shown in Table I and by the smoothed curve of Fig. 1. For the transition temperature Piper's mean value of 64.6° is assumed to be correct. On cooling through this temperature a marked change in the appearance of the film between the Abbe prisms is noted (the same changes are seen in a film formed on a slide under a cover glass): the texture changes from fine-grained to coarse-grained, and air bubbles appear, probably because of the contraction in volume. At the transition temperature both refractive indices change by 0.018 unit.

TABLE I

REFRACTIVE INDICES OF DICETYL IN THE LIQUID AND TWO SOLID PHASES

Temp., °C.	ε		ω
20	1.5645		1.5148
30	1.5625		1.5126
40	1.5593		1.5096
50	1.5553		1.5053
60	1.5500		1.5000
64.6	1.5472		1.4971
64.6	1.5290		1.4788
67.5	1.5270		1.4768
69.6	1.5257		1.4756
69.6		1.4358	
75		1.4338	
80		1.4325	

It will be noted that the birefringence of a solid dicetyl film is the same, about 0.050, in its two phases, and does not vary sensibly with temperature. It might have been expected to be higher for the high temperature form, for Piper and his co-workers found the molecular axes to be perpendicular to the basal plane in the high temperature or A-form (d_{001} 42.33 Å.), but to have some obliquity thereto in the low temperature or C-form (d_{001} 37.8 Å.).

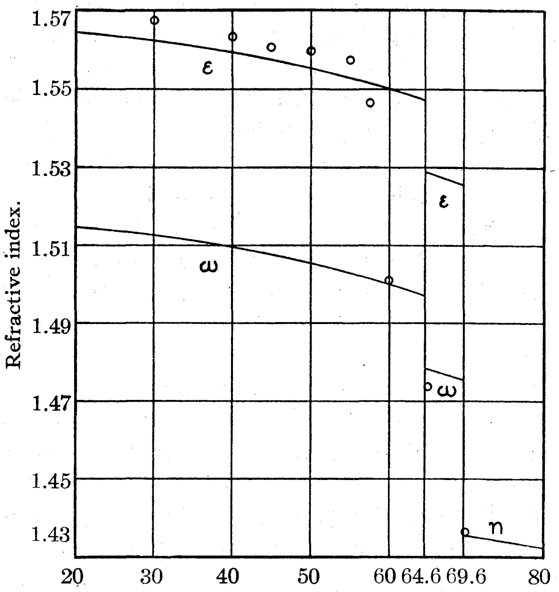

Fig. 1.—Refractive indices of dicetyl in the liquid and two solid phases.

The circles in Fig. 1 represent the measurements of Seyer and Fordyce. It is seen that while their points agree with the interpretation that dicetyl has a transition about 5° below the melting point, their conclusion that a transition occurs at 55° is forced and erroneous.

Summary

The simple procedure is described for measuring, by means of a total reflection refractometer equipped with a cap polarizer, the refractive indices of materials which solidify to form transparent uniaxial films. The dimorphism of solid dicetyl is demonstrated by refractometric measurements, and approximate values of its optical constants are given over a range of temperatures.

BOSTON, MASS. RECEIVED FEBRUARY 6, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

On 1,2- and 1,4-Addition. I. The 1,4-Addition of Potassium Isocyanide[1]

BY ARTHUR MICHAEL AND NATHAN WEINER

The synthesis of β-cyano ketones, esters and nitriles through the action of potassium isocyanide on the corresponding α,β-ethylenic ketones, esters and nitriles is a general reaction.[2] It has been and is assumed that it proceeds by addition of liberated hydrocyanic acid to the α,β-ethylenic carbons, analogously to the addition of strong mineral acids,[3] or primarily by the union of the cyano ion to the β-carbon.[2i] However, hydrogen cyanide[4] functions very weakly acidic ($k^{25}_{\mathrm{HCN}} = 7.2 \times 10^{-10}$), and the facility with which an acid adds to an ethylene group is in direct relation to the strength of the acid.[5] Obviously, so weak an acid as hydrogen cyanide cannot add to ethylenic carbons. Further, the supposed addition of hydrogen cyanide occurs only in the presence of alkali isocyanide and to compounds containing an ethylenic group conjugated with a carbonyl, carbalkoxyl, nitro or nitrile group. The synthesis of pyrotartaric dinitrile from an allyl halide, or allyl cyanide, and isocyanide may seem an exception. However, the reactions were carried out in a partially aqueous medium,[2a,6] in which alkali isocyanides show strongly alkaline properties. Such conditions favor the allyl into propylene shift and allyl cyanide undoubtedly first undergoes a change to crotononitrile. That the formation of pyrotartaric dinitrile proceeds in this manner was proved by the recovery of considerable unchanged allyl cyanide after protracted boiling with isocyanide in absolute methyl alcoholic solution and that no dinitrile was formed under these conditions. Bredt and Kallen[2c] attributed the function of the isocyanide to the formation of *nascent* hydrogen cyanide; but its greater reactivity could be connected only with a greater heat of reaction and hydrogen cyanide does not add even at higher temperatures. Lapworth[2g] believed the reaction proceeds primarily through the —CN ion of a complex salt, formed from hydrogen cyanide and isocyanide, and that it proceeds analogously to Thiele's view, by union of hydrogen with carbonyl oxygen and a cyano group with the β-Δ-carbon; although Thiele[2d] accepted 1,2-addition and his 1,4-viewpoint had been shown untenable.[7a] Lapworth[2i] also thought that the addition may occur to an unconjugated ethylene group, since an analogous addendum, sodium acid sulfite, unites with the α,β-Δ-carbons of cinnamyl alcohol. If the sulfite, $NaSO_2OH$,[7b] added as $NaSO_2O$— and H— a poorly neutralized sulfite derivative would be formed, but, if the H— joins the α-Δ-carbon, with migration of sodium to its place, and the sulfur radical the β-Δ-carbon, then in the well-neutralized sodium sulfonate the maximum possible energy degradation is attained. Obviously, no connection exists between the mechanisms of the two addenda. Recently, Ingold[8] compared the hydrogen cyanide addition to α,β-Δ-esters to that of enolates; the latter and isocyanide providing the anions and the cations uniting with the carbonyl oxygen. This comparison is not tenable; the additivity of malonic ester depends upon the free chemical energy in the ethylenic group,[9] and the pure sodium enolate adds instantaneously in organic solvents with low dielectric and dissociating constants; further the addition does not depend upon an imagined dissociation of the addenda, but upon the possible formation of a new, chemically better neutralized, system.[10] The

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(1) The correct, scientific name and structure of "potassium cyanide" is used in this paper. See *Ann.*, **364**, 64 (1908), for literature.

(2) (a) Claus, *Ann.*, **191**, 33 (1878); (b) Rupe and Schneide, *Ber.*, **28**, 960 (1895); (c) Bredt and Kallen, *Ann.*, **293**, 342 (1896); (d) Thiele and Meisenheimer, *ibid.*, **306**, 247 (1899); (e) Ruhemann and Watson, *J. Chem. Soc.*, **85**, 1454 (1904); Lapworth and coworkers, *ibid.*, (f) **85**, 1065, 1284, 1355 (1904); (g) **83**, 995 (1903); (h) **89**, 1868 (1906); (i) **121**, 49 (1922); (j) **127**, 560 (1925); (k) Hope, *ibid.*, **121**, 2223 (1922).

(3) Michael and Carlson, THIS JOURNAL, **57**, 1268 (1935); Michael and Weiner, *ibid.*, **58**, 294 (1936).

(4) According to Michael [*Ber.*, **34**, 4030, footnote 3 (1901)], hydrogen cyanide contains an extremely small content of the corresponding isocyanide (HNC), in reversible equilibrium with the nitrilic form. E. H. Usherwood [*J. Chem. Soc.*, **121**, 1604 (1922)] concluded from specific heat measurements that gaseous hydrogen cyanide contains several tenths of one per cent. of the acidic form. K. H. Meyer [*Ber.*, **54**, 1709 (1921)], apparently under the belief that an appreciable proportion of the latter is present, endeavored, unsuccessfully, to isolate it by fractionation. The formation of hydroxynitriles from aldehydes and aqueous hydrogen cyanide should proceed through the more energetic acidic form and the addition forms a nitrile because of the greater affinity of the formyl carbon for the C than for the N of HNC and that this course leads to the maximum degradation of energy.

(5) Michael and Brunel, *Am. Chem. J.*, **41**, 118 (1909).

(6) Wislicenus and Euler, *Ber.*, **28**, 2952 (1895); Pomeranz, *Ann.*, **351**, 357 (1907).

(7) Michael, *J. prakt. Chem.*, (a) **60**, 467, (b) 305 (1899).

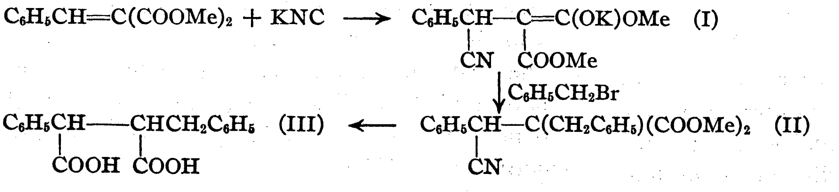
(8) Ingold and Bloom, *J. Chem. Soc.*, 2765 (1931).

(9) Michael, *J. prakt. Chem.*, **36**, 114 (1887).

(10) Michael, *Ber.*, **37**, 22 (1904); Michael and Cobb, *Ann.*, **363**, 64 (1908).

theoretical importance of 1,2-addition of hydrogen cyanide has long been and is still emphasized as proving that no relation exists between 1,4-addition and structure; for example, Hinrichsen[11] in 1902 and Hückel[12] in 1934. However, the following experimental results prove conclusively that hydrogen cyanide is not essential for, nor does it enter into, these reactions, and that they take place exclusively by 1,4-addition, through the isocyanide; thus invalidating all the above speculations.

Previous investigators of the isocyanide reaction used aqueous ethyl alcohol, as the salt is sparingly soluble in absolute alcohol. Under these conditions it seemed possible that primarily formed intermediates may be decomposed by the action of water. Bredt and Kallen[2c] found that a mixture of aqueous potassium isocyanide and an alcoholic solution of benzalmalonic ester, followed by hydrochloric acid, gave β-cyanobenzylmalonic ester and the ester in alcoholic solution with an aqueous solution of isocyanide at 60° gave β-cyanophenylpropionic ester. These results were explained when absolute methanol was used as a solvent. The addition of isocyanide to ester proceeds so rapidly that the salt, suspended in a small volume of absolute methanol, dissolves almost immediately upon addition of ester and a good yield of potassium compound quickly separates, which represents an equimolecular addition product of isocyanide and ester. Acidification of this potassium derivative yielded β-cyanobenzylmalonic ester (IV), identical with the compound prepared according to Bredt and Kallen,[2c] but in far better yield. The potassium compound (I) is an enolate; it reacts with benzyl bromide to give the α-benzyl derivative (II), the structure of which is established by hydrolysis to α-benzyl-β-phenylsuccinic acid (III):

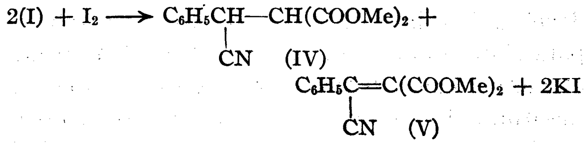


$$\mathrm{C_6H_5CH{=}C(COOMe)_2 + KNC \longrightarrow \underset{CN}{C_6H_5CH}-\underset{COOMe}{C}{=}C(OK)OMe}\quad (I)$$

$$\Big\downarrow \mathrm{C_6H_5CH_2Br}$$

$$\mathrm{\underset{COOH}{C_6H_5CH}-\underset{COOH}{CHCH_2C_6H_5}}\ (III) \longleftarrow \mathrm{\underset{CN}{C_6H_5CH}-C(CH_2C_6H_5)(COOMe)_2}\quad (II)$$

With iodine, instead of the usual C-copulation, equivalent amounts of β-cyanobenzylmalonic ester (IV) and β-cyanobenzalmalonic ester (V) are formed



$$2(I) + I_2 \longrightarrow \mathrm{\underset{CN}{C_6H_5CH}-CH(COOMe)_2}\ (IV) + \mathrm{\underset{CN}{C_6H_5C}{=}C(COOMe)_2} + 2KI\ (V)$$

The reaction follows in the first stage the mechanism suggested for the coupling of enolates,[13] which postulates the intermediate formation of an α-iodo compound and its interaction with unchanged enolate. However, the α-iodo compound, $C_6H_5CH(CN)CI(COOMe)_2$ (VI), contains the halogen in the β-position to the nitrile group and belongs to a class of β-derivatives from which halogen hydride is separated with great ease. As (VI) is formed, hydrogen iodide is eliminated by unchanged enolate and (IV) and (V) therefore appear in equal amounts.

Since the addition of potassium isocyanide to benzalmalonic ester is very rapid[14] and the primary product is an enolate, the explanation of Bredt and Kallen's results is apparent. In the experiment with aqueous alcohol at 60°, the enolate was formed practically at once and was changed upon heating into $C_6H_5CH(CN)CH(COOK)COOEt$, which upon further heating, analogously to similarly structured compounds,[15] broke up into potassium bicarbonate and β-cyanophenylpropionic ester. In the reaction at room temperature, the enolate had formed before the addition of mineral acid, which simply set free a poor yield of the corresponding enolic derivative.

The above reaction is an ideal illustration of the interpretation of 1,4-addition from Michael's standpoint.[16] Benzalmalonic ester contains a malonic ester group, without the essential α-hydrogen necessary to yield an enolate; the carbonyl oxygen of a carbmethoxy group has, however, a

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(11) Hinrichsen, *Ann.*, **320**, 60 (1902).

(12) "Hückel, Theoretische Grundlagen der organischen Chemie," 1934, pp. 347, 351.

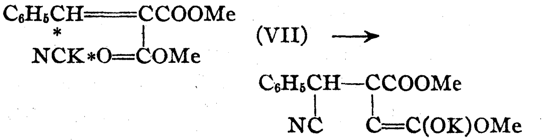
(13) Michael, *J. prakt. Chem.*, **60**, 286 (1899).

(14) So rapid, that an attempt to measure the rate of disappearance of potassium isocyanide by titration was unsuccessful; more than 50% of the isocyanide had disappeared before the first titration could be carried out.

(15) Michael, *J. prakt. Chem.*, **72**, 544 (1906).

(16) Michael, *J. prakt. Chem.*, **60**, 299, 467, 470, 481 (1899); **68**, 512, 521 (1903); **79**, 418 (1909). A theoretical development of 1,4-addition, based upon the chemical affinity and the chemical energy of the atoms involved in the reacting chemical systems, and a theoretical and exper imental refutation of Thiele's [*Ann.*, **306**, 89 (1899)] mechanical speculations. Straus [*Ber.*, **42**, 2866 (1909)] took exception to the implication of the affinity factor, since he found that Br_2 added 1,2 and Wieland [*Ann.*, **360**, 311 (1908)] that nitrogen tetroxide added NO_2 in 1,4-position to 1,4-diphenylbutadiene. However, Wieland's conclusion is based upon inconclusive experimental results and the more important experiments could not be repeated in this Laboratory.

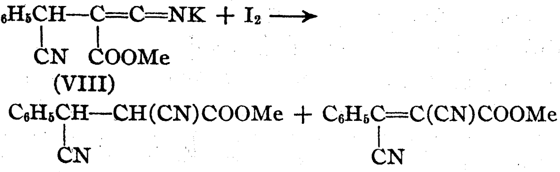
developed affinity for the slightly neutralized potassium atom of the isocyanide and a strong attraction exists between it and the respective, unsaturated oxygen. Further, the β-Δ-carbon of the ester shows the necessary free chemical energy and affinity, *i. e.*, the chemical potential,[17] to unite with the cyano group. The first formed, cyclic, polymolecule[18] (VII) passes over into the β-cyano enolate (I)



$$\begin{array}{l} C_6H_5CH{=\!=}CCOOMe \\ \quad {*}\qquad\;\; | \\ NCK{*}O{=}COMe \end{array} \quad (VII) \longrightarrow \quad \begin{array}{l} C_6H_5CH{-}CCOOMe \\ \quad\; |\qquad\; | \\ \;\;NC\quad\; C{=}C(OK)OMe \end{array}$$

(I)

For, the β-Δ-carbon has a far more developed affinity for the carbon than the nitrogen of the addendum and the introduction of the decidedly negative cyano group leads to a far better neutralized enolate (I) than would **the** basic isocyano group. The combination of the ester molecule, loaded with free, negative chemical energy at Δ-oxygens and Δ-carbons, and the isocyanide, with free, positive, chemical energy in large excess, to form the almost neutral enolate molecule, represents the possible maximum degradation of energy of the original chemical system and, therefore, the inevitable course of the chemical change. The above considerations apply also to the reaction between benzalcyanoacetic ester and isocyanide. This facile reaction leads to the iminolate of β-cyanobenzylcyanoacetic ester (VIII),[19] which with iodine gives equimolecular amounts of β-cyanobenzylcyanoacetic ester (IX) and β-cyanobenzalcyanoacetic ester (X)



$$\begin{array}{l} C_6H_5CH{-}C{=}C{=}NK + I_2 \longrightarrow \\ \qquad |\qquad | \\ \quad\; CN\;\; COOMe \\ \qquad (VIII) \\ C_6H_5CH{-}CH(CN)COOMe + C_6H_5C{=}C(CN)COOMe \\ \qquad | \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \quad\;\; CN \qquad\qquad\qquad\qquad\qquad\qquad CN \\ \qquad (IX) \qquad\qquad\qquad\qquad\qquad\quad (X) \end{array}$$

To confirm these views further, the reaction between fumaric ester and potassium isocyanide was examined under varied conditions. In 90% methanol reaction occurs readily at room temperature; after acidification, 1-cyano-2,3,4-carbmethoxybutane (XV), along with considerable acid fumaric ester, were obtained. In absolute methanol at room temperature, after acidification, the products were methoxysuccinic ester and 2-cyano-3,4,5-carbmethoxycyclopentanone (XVII), the relative proportions depending on the time, the methoxy ester disappearing for the cyclopentanone derivative (XVII) on longer standing. Finally, in boiling absolute methanol, only the cyclopentanone derivative (XVII) was formed in appreciable yield. These relations support the proposed 1,4-mechanism. In methyl alcohol, potassium isocyanide is undoubtedly in equilibrium with potassium methylate and the presence of the methylate brings about reversible formation of methoxysuccinic ester.[20] The reaction is, therefore, competitive between isocyanide and methanol for addition to fumaric ester. Without water, enolate (XI) should mainly rearrange to the much better neutralized iminolate (XII) with some of the corresponding enolate (XIII), which undergo the enolate addition[21] with unchanged fumaric ester, to form the potassium derivative of 1-cyano-1,2,3,4-carbmethoxybutane (XIV).[22] In absolute methanol the new potassium derivative undergoes a Dieckmann condensation and the iminolate (XVI) yields with mineral acid the cyclopentanone derivative (XVII).[23] In the presence of water, however, even at room temperature, the iminolate ester (XIV) is partially saponified and, in the subsequent manipulation, it is decarboxylated to (XV).

When the metal is insufficiently neutralized in the KNC addition product, the following phase of the reaction should, as it does, proceed slowly and, under such conditions, the product behaves exactly like other imperfectly neutralized enolates toward compounds of the type RCH═CHCOOR. The formation of the more complex addition products in the isocyanide reactions is, therefore, experimental proof that, in the first phase, they add normally to form enolates and the addition reaction is experimental evidence that the isocyanide has the iminolate structure, *i. e.*, KNC.

Michael and Schulthess[24] showed that sodium malonic enolate added to citraconic ester in ether solution and gave the expected addition product;

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[17] Michael, *Ann.*, **363**, 21 (1908); THIS JOURNAL, **32**, 990 (1910).

[18] Michael and Carlson, *ibid.*, **57**, 160 (1935), for use of asterisk and graphic illustrations.

[19] There can be no doubt that the metal is attached mainly to nitrogen. The term iminolate is suggested for a compound containing the ═C═Nmetal group.

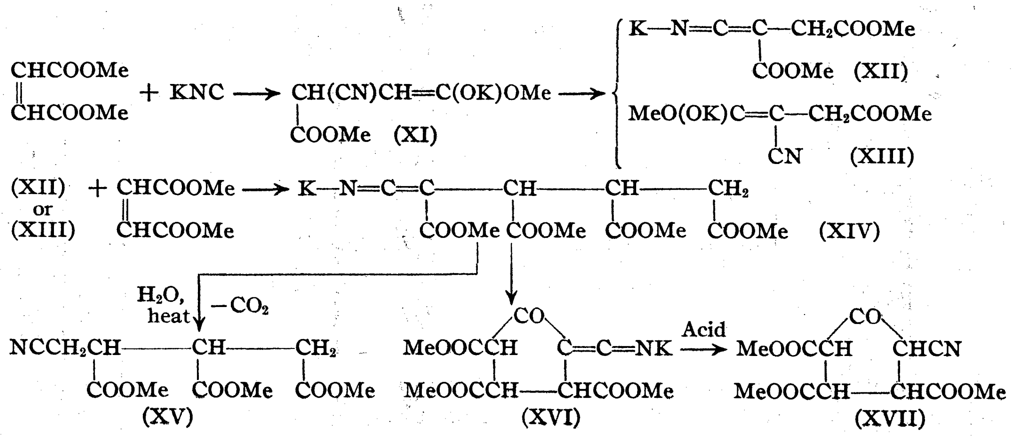
[20] Purdie and Marshall, *J. Chem. Soc.*, **59**, 469 (1886).

[21] See Michael and Ross, THIS JOURNAL, **53**, 1150 (1931), for literature.

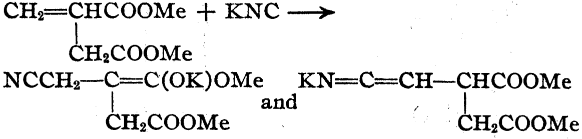
[22] V. Auwers and Jacob, *Ber.*, **27**, 1114 (1894).

[23] V. Auwers, *ibid.*, **26**, 364 (1893).

[24] Michael and Schulthess, *J. prakt. Chem.*, **45**, 55 (1892).



but in alcoholic solution[25] a condensation occurred with loss of alcohol and the enolate of a cyclic ketone derivative was formed. Hope[26] proved that citraconic ester first isomerized to itaconic ester and that the ketone was a cyclopentanone derivative. In absolute methanol, at room temperature, citraconic methyl ester and isocyanide gave, after acidification, two products; one by addition of methyl alcohol and a second with the empirical constitution $C_7H_9O_4N$, their relative proportions depending on time; $C_7H_9O_4N$ being formed with disappearance of the methoxy ester. In boiling methanol only $C_7H_9O_4N$ could be isolated. After heating with acid, or base, it yielded tricarballylic acid, or its salt, which showed that citraconic ester must have rearranged to itaconic ester, before the addition of isocyanide.

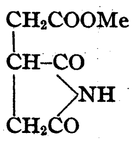


$$CH_2{=}\underset{\displaystyle\overset{|}{CH_2COOMe}}{C}HCOOMe + KNC \longrightarrow$$

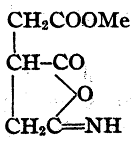
$$NCCH_2{-}\underset{\displaystyle\overset{|}{CH_2COOMe}}{C}{=}C(OK)OMe \quad \text{and} \quad KN{=}C{=}CH{-}\underset{\displaystyle\overset{|}{CH_2COOMe}}{C}HCOOMe$$

(XVIIIa) (XVIIIb)

The resulting product (XVIIIa, b) underwent rearrangement and condensation to give an imidic (XIX) or imidolactonic (XX) derivative

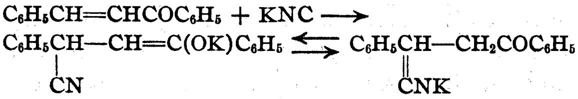


(XIX)



(XX)

β-Cyanobenzylacetophenone (XXI) has been prepared by the action of the isocyanide on benzalacetophenone under varied conditions[2b,27] Hann and Lapworth[27a] treated the ketone, in 92% alcohol, with two equivalents of potassium isocyanide and one equivalent of diluted acetic acid. Along with (XXI) a small yield of compound, $C_{31}H_{23}ON$,[27a] was obtained; it was also formed by condensation of benzalacetophenone with (XXI) by strong alkali. In boiling absolute methanol, benzalacetophenone reacts with isocyanide to give, directly, $C_{31}H_{25}O_2N$, which, with alkali or acid, lost water and gives Hann and Lapworth's $C_{31}H_{23}ON$. The first stage of the reaction evidently results in enolate (XXII), in which the metal is poorly neutralized and which should rearrange to a mixture containing, largely, the still imperfectly neutralized iminolate (XXIII)

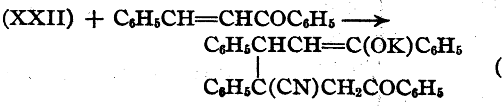


$$C_6H_5CH{=}CHCOC_6H_5 + KNC \longrightarrow$$

$$C_6H_5\underset{\displaystyle\overset{|}{CN}}{C}H{-}CH{=}C(OK)C_6H_5 \rightleftarrows C_6H_5\underset{\displaystyle\overset{\|}{CNK}}{C}H{-}CH_2COC_6H_5$$

(XXII) (XXIII)

The potassium enolate (XXII) can attain a better neutralization by reacting with another molecule of benzalacetophenone, but iminolate (XXIII) cannot do so. The reaction, therefore, proceeds through enolate (XXII), which is reformed as it disappears in the addition process



$$(XXII) + C_6H_5CH{=}CHCOC_6H_5 \longrightarrow \begin{array}{l} C_6H_5CHCH{=}C(OK)C_6H_5 \\ \quad\;\; | \\ C_6H_5C(CN)CH_2COC_6H_5 \end{array}$$

(XXIV)

This formula (XXIV) is the enolate of the structure suggested by Hann and Lapworth for the hitherto unisolated, second phase of the addition process. Since the cyclic intramolecular condensation product is formed from $C_{31}H_{25}O_2N$ in alkaline solution, *i. e.*, from the enolate, the reaction can proceed in one direction, not in two, as Hann and Lapworth assume. However, two isomeric compounds of the formula $C_{31}H_{23}ON$ may be formed, through aldolization, with ring

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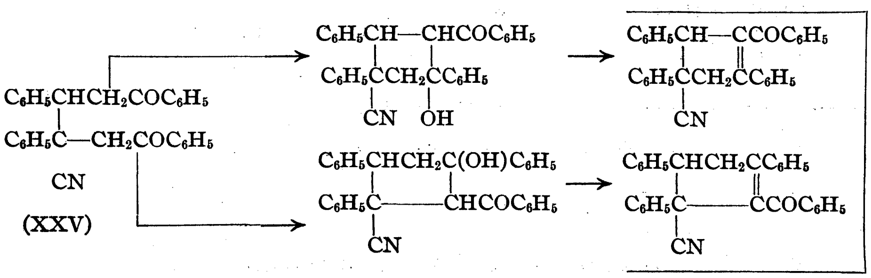
[25] Michael, *Ber.*, **33**, 3757 (1900).

[26] Hope, *J. Chem. Soc.*, **101**, 902 (1912).

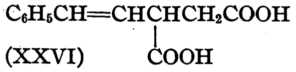
[27] (a) Hann and Lapworth, *ibid.*, **85**, 1358 (1904); (b) Lapworth and Wechsler, *ibid.*, **97**, 38 (1910).

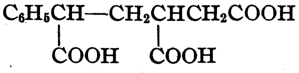
formation and elimination of water, of the corresponding free compound

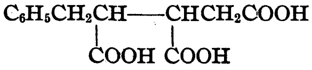


We attempted, without success, to prove definitely the structures of $C_{31}H_{25}O_2N$ and $C_{31}H_{23}ON$. The first compound resists hydrolysis with concentrated acid and alkali, but is dehydrated to $C_{31}H_{23}ON$, which is, as stated above, probably a ring compound. Hydrolysis in sealed tubes with concentrated hydrochloric acid, at temperatures from 140 to 200°, gave only intractable tars, and treatment with chromic anhydride in glacial acetic acid, or potassium permanganate in acetone, brought about dehydration to $C_{31}H_{23}ON$. In agreement with Hann and Lapworth, we found the latter compound very resistant to hydrolysis or oxidation, reaction taking place under very drastic conditions and giving nothing more significant than benzoic acid or acetophenone. Suspended in glacial acetic acid, $C_{31}H_{25}O_2N$ gave $C_{31}H_{22}ONBr$ with bromine, by substitution of one of the hydrogens for bromine and elimination of water. This compound is apparently not directly related to $C_{31}H_{23}ON$ since it could not be produced by bromination of that compound. The bromination product lost hydrogen bromide by the action of sodium methylate and gave a bright yellow compound $C_{31}H_{21}ON$. This was oxidized by chromic acid to give a poor yield of $C_{24}H_{17}ON$.

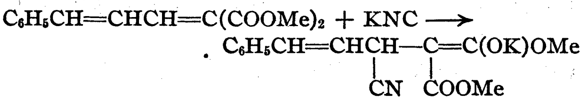
Cinnamalmalonic ester and isocyanide reacted in absolute methanol at room temperature and gave, after acidification, $C_{29}H_{29}O_8N$, formed by union of the primary β-cyano enolate with unchanged ester. In aqueous alcohol, with isocyanide and ester in molecular proportions, by subsequent hydrolysis, Thiele and Meisenheimer[2d] obtained styrylsuccinic acid (XXVI). With three moles of isocyanide to one of ester a product was obtained which on hydrolysis gave tribasic acid (XXVII).

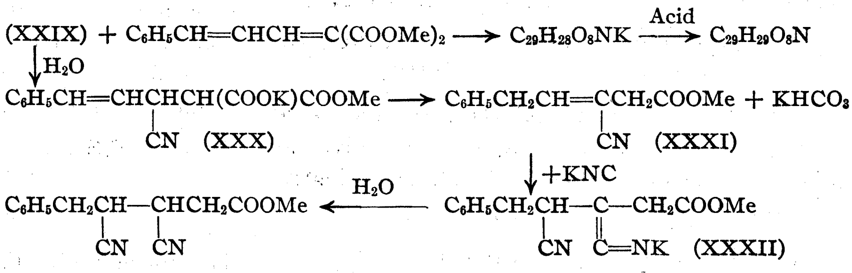

$$C_6H_5CH{=}CH\underset{COOH}{\underset{|}{C}H}CH_2COOH$$
(XXVI)


$$C_6H_5\underset{COOH}{\underset{|}{C}H}-CH_2\underset{COOH}{\underset{|}{C}H}CH_2COOH$$
(XXVII)


$$C_6H_5CH_2\underset{COOH}{\underset{|}{C}H}-\underset{COOH}{\underset{|}{C}H}CH_2COOH$$
(XXVIII)

Thiele and Meisenheimer assumed that the reaction leading to (XXVI) was 1,2-addition of hydrogen cyanide, and to (XXVII), first 1,4- and then 1,2-addition. Duff and Ingold[28] proved the correct structure, (XXVIII), the formation of which was explained by assuming α,β-addition to give $C_6H_5CH{=}CHCH(CN)CH(COOR)_2$, which rearranged to $C_6H_5CH_2CH{=}C(CN)CH(COOR)_2$, and which by a second β,γ-addition of hydrogen cyanide yielded the dinitrile $C_6H_5CH_2CH(CN)CH(CN)CH(COOR)_2$ corresponding to (XXVIII). Since hydrogen cyanide does not add, the primary product must be enolate (XXIX), which under the first experimental conditions gave potassium salt (XXX). With excess of isocyanide (XXX) rearranges to (XXXI), which by 1,4-addition of isocyanide forms iminolate (XXXII). Without water, enolate (XXIX) is stable and adds to unchanged ester, forming $C_{29}H_{28}O_8NK$.


$$C_6H_5CH{=}CHCH{=}C(COOMe)_2 + KNC \longrightarrow C_6H_5CH{=}CH\underset{CN}{\underset{|}{C}H}-\underset{COOMe}{\underset{|}{C}}{=}C(OK)OMe$$
(XXIX)



In absolute methanol, isocyanide acts slowly and incompletely on crotonic ester, giving enolates of complex, high boiling esters, probably formed by interaction of primarily formed enolates with unchanged ester. In the presence of water, the enolate is hydrolyzed to the corresponding salt, thus preventing secondary reactions, and by hydrolysis pyrotartaric acid was obtained.[2i]

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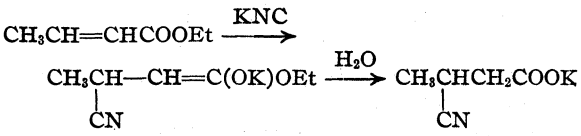
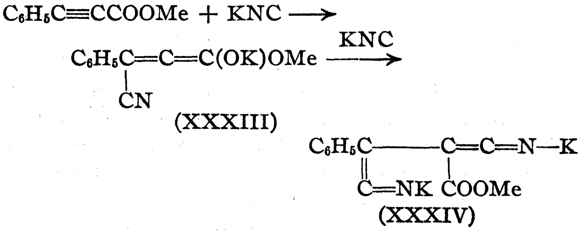
[28] Duff and Ingold, *J. Chem. Soc.*, 87 (1934).



$$CH_3CH{=}CHCOOEt \xrightarrow{KNC}$$

$$CH_3\underset{\underset{CN}{|}}{C}H{-}CH{=}C(OK)OEt \xrightarrow{H_2O} CH_3\underset{\underset{CN}{|}}{C}HCH_2COOK$$

Cobb[29] heated phenylpropiolic ester, isocyanide and aqueous alcohol and isolated $C_6H_5CH(CN)CH_2CN$ with potassium bicarbonate obviously formed by decomposition of $C_6H_5CH(CN)C(CN){=}C(OK)OEt$. In boiling absolute methyl alcohol, phenylpropiolic methyl ester reacts with isocyanide to give after acidification, mainly a mixture of β-methoxycinnamic ester and benzoylacetic ester and about 20% of β-cyanobenzylcyanoacetic ester (IX). The first-formed β-methoxycinnamic ester undoubtedly adds a second molecule of alcohol to form $C_6H_5C(OCH_3)_2CH_2COOMe$,[30] which is converted by isocyanide into benzoylacetic ester enolate. In aqueous alcohol, at room temperature, the addition of methanol is suppressed in favor of isocyanide, and a better yield of (IX) is obtained by the way of the enolate (XXIII) and the diiminolate (XXXIV).



$$C_6H_5C{\equiv}CCOOMe + KNC \longrightarrow$$

$$C_6H_5\underset{\underset{CN}{|}}{C}{=}C{=}C(OK)OMe \xrightarrow{KNC}$$

(XXXIII)

$$C_6H_5\underset{\underset{C=NK}{\|}}{C}{-\!-\!-}\underset{\underset{COOMe}{|}}{C}{=}C{=}N{-}K$$

(XXXIV)

The di-iminolate (XXXIV) contains two potassium atoms in different states of neutralization; that at the cyanoacetic ester grouping is better neutralized than that attached to the β-cyano group, and the latter yields, with water, the free nitrile group and potassium hydroxide which saponifies unchanged phenylpropiolic ester.

Malonic enolates add to monobasic α,β-acetylenic esters, with migration of the metal from the malonic to the mono-carbmethoxy group;[31] to this new type of stable enolates belongs (XXXIII), which also derived from an α,β-Δ-ester through enolization of the α-Δ-CH group. Earlier attempts to prepare such enolates directly from esters and sodium[32] led to the formation of enolates of depolymerized esters; in recent experiments, using a solution of sodium in liquid ammonia, we obtained analogous results.

Experimental

Action of Potassium Isocyanide on Allyl Cyanide.—The allyl cyanide (6.7 g.), b. p. 117.5–119°, was added to a suspension of 6.5 g. of potassium isocyanide in 50 cc. of absolute methanol and boiled. At the end of four hours the solution started to turn yellow and at the end of twenty-four, when the reaction was stopped, the solution had become dark brown. The solvent was removed as completely as possible on the water-bath and the residue diluted with 100 cc. of dry ether. The precipitate was filtered and the filtrate was concentrated, leaving a residue of 6.0 g. This was distilled and yielded 5.5 g. of allyl cyanide, b. p. 115–120°.

β-Cyanobenzylmalonic Dimethyl Ester, (I) and (IV), (a).—Benzalmalonic dimethyl ester (5.5 g.) was added to a suspension of 1.63 g. of potassium isocyanide in 20 cc. of boiling absolute methanol. The salt dissolved immediately; one-half of the solvent was distilled off, which resulted in the separation of a voluminous, white, crystalline potassium compound. One hundred cc. of dry ether was added and the mixture cooled in an ice-bath. The solid was filtered, washed repeatedly with ether and dried *in vacuo* at 100°; yield 7.0 g. (100%).

Anal. Calcd. for $C_{13}H_{12}O_4NK$ (I): K, 13.7. Found: K, 13.4.

The potassium compound was suspended in ether, dilute acid added and the mixture shaken until solution was complete. The dried solution was freed of ether and the colorless residual oil was dissolved in an equal volume of methanol and cooled to −20°, when it completely solidified; yield 6.0 g. (100%). The compound was recrystallized by dissolving in the minimum volume of methanol at room temperature and cooling in a freezing mixture; it separated in rosets of needles, m. p. 47.5–48.5°.

Anal. Calcd. for $C_{13}H_{13}O_4N$ (IV): C, 63.16; H, 5.26. Found: C, 63.25; H, 5.43.

(b).—Benzalmalonic dimethyl ester (5.5 g.) was dissolved in 50 cc. of methanol and a solution of 1.65 g. of potassium isocyanide in 20 cc. of water was added. The solution stood ten minutes, 3 cc. of concentrated hydrochloric acid was added, and then allowed to stand for twenty-four hours. It was diluted with sufficient water to cause precipitation of an oil, which was extracted with ether and the residue from the dried ether solution was dissolved in methanol. By seeding and cooling to −20°, 3 g. of a solid separated, identical with the β-cyanobenzylmalonic ester (IV) obtained above.

α-Benzyl-β-cyanobenzylmalonic Dimethyl Ester (II).—Potassium enol β-cyanobenzylmalonic ester (I), (12.2 g.), was suspended in 75 cc. of dry toluene and boiled with 7.3 g. of benzyl bromide for three hours. The solid was separated by centrifuging and was washed repeatedly with ether; weight 10.2 g. (theoretical for potassium bromide, 5.1 g.). The solid was suspended in ether, shaken with dilute acid, and the dried ether solution yielded, on concentration, 5.5 g. of β-cyanobenzylmalonic ester (IV). The ether–toluene solution was concentrated *in vacuo* and the residue taken up in ether. Dilution with petroleum ether and cooling to −20° yielded 4 g. of crystalline solid, which, after recrystallization from ether–petroleum ether, melted at 117.5–118°.

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(29) Cobb, *Am. Chem. J.*, **45**, 604 (1910).

(30) See Michael and Bucher, *Ber.*, **29**, 1793 (1896).

(31) Gidvani, Kon and Wright, *J. Chem. Soc.*, 1027 (1932); Gidvani and Kon, *ibid.*, 2443; Farmer, Ghosal and Kon, *ibid.*, 1804 (1936).

(32) Michael, *Ber.*, **33**, 3766 (1900).

Anal. Calcd. for $C_{21}H_{19}O_4N$ (II): C, 71.22; H, 5.64. Found: C, 70.90; H, 5.56.

α-Benzyl-β-phenylsuccinic Acid (III).—One gram of (II) was heated in a sealed tube with 25 cc. of concentrated hydrochloric acid at 200° for five hours. The resulting solution was extracted with ether and the ether washed with saturated sodium bicarbonate solution. Acidification of the washings, extraction with ether and concentration of the dried ether solution yielded 0.6 g. of acid, which, after recrystallization from 30% methanol, melted at 175–176° and had a neutral equivalent of 144. Calcd. for $C_{17}H_{16}O_4$: (dibasic) 142. It is therefore α-benzyl-β-phenylsuccinic acid.[33]

β-Cyanobenzalmalonic Dimethyl Ester (V).—Potassium enol β-cyanobenzylmalonic ester (I), (10.5 g.) was suspended in 75 cc. of boiling toluene and a solution of 4.6 g. of iodine in 25 cc. of toluene was added dropwise. The iodine was decolorized immediately until the last drop, which colored the supernatant liquor faintly pink. The potassium iodide was separated by centrifuging and was washed repeatedly with ether; weight 6.1 g. (theoret.). The solution and washings were concentrated *in vacuo*, the residue was dissolved in ether, diluted with petroleum ether and cooled to −20°. A small amount of solid crystallized out and repeated concentration of the mother liquor and cooling finally yielded 3.85 g. of this compound, leaving 4.25 g. of brown oil. The solid was recrystallized from ether–petroleum ether, giving flat needles, m. p. 74°.

Anal. Calcd. for $C_{13}H_{11}O_4N$ (V); C, 63.67; H, 4.47; mol. wt., 245. Found: C, 64.17, 63.81; H, 4.36, 5.02; mol. wt. (Pirsch, camphor), 247, 250.

One gram of this compound was shaken with hydrogen in the presence of 0.05 g. of Adams catalyst and absorbed 120 cc. (one mole) in four minutes. The filtered solution yielded β-cyanobenzylmalonic ester (IV).

The residual brown oil from the iodine reaction was freed of ether and dissolved in an equal volume of methanol and cooled to −20°. Inoculation with a seed crystal caused separation of 4 g. of β-cyanobenzylmalonic ester (IV).

β-Cyanobenzylcyanoacetic Methyl Ester, (VIII) and (IX).—Benzalcyanoacetic methyl ester (9.35 g.) was added to a suspension of 3.25 g. of potassium isocyanide in 25 cc. of absolute methanol. The salt disappeared almost immediately after warming the mixture but no solid separated when half the solvent was distilled off. The residual solution, cooled and diluted with 100 cc. of dry ether, gave a crystalline potassium compound. This was filtered, washed repeatedly with ether and dried *in vacuo* at 100°; yield 12 g. (100%).

Anal. Calcd. for $C_{12}H_9O_2N_2K$ (VIII): K, 15.5. Found: K, 14.7.

The potassium compound was suspended in ether and shaken with dilute acid until completely decomposed. The resulting compound was only sparingly soluble in ether and was filtered, washed with ether and cold methanol. The washings were combined with the ether layer, dried and concentrated, yielding a small additional quantity of the compound; yield 10.5 g. (100%). After recrystallization from benzene it melted at 107–108°.

Anal. Calcd. for $C_{12}H_{10}O_2N_2$ (IX): C, 67.30; H, 4.67. Found: C, 67.21; H, 4.89.

β-Cyanobenzalcyanoacetic Methyl Ester (X).—Potassium enol β-cyanobenzylcyanoacetic ester (VIII), (12.6 g.), was suspended in 50 cc. of dry toluene and a solution of 6.3 g. of iodine in 50 cc. of toluene was added dropwise to the boiling mixture. When the addition was completed the hot solution was filtered and the salt washed with hot benzene. The combined filtrate and washings was washed with sodium thiosulfate solution, dried and concentrated to about 10 cc. Dilution with ether and petroleum ether gave 7.0 g. of solid and concentration of the mother liquor yielded an additional gram. The solid was extracted several times with ether, leaving undissolved 3.8 g. of β-cyanobenzylcyanoacetic ester (IX). The ether was concentrated, and, after 0.2 g. of (IX) was obtained, dilution with petroleum ether gave 3.8 g. of a new substance. This was recrystallized from ether–petroleum ether and melted at 87–88°.

Anal. Calcd. for $C_{12}H_8O_2N_2$ (X): C, 67.93; H, 3.77. Found: C, 67.91; H, 4.36.

Catalytic reduction of this compound gave a quantitative yield of β-cyanobenzylcyanoacetic ester (IX).

1 - Cyano - 2,3,4 - carbmethoxybutane (XV).—Fumaric methyl ester (7.2 g.) was suspended in a solution of 3.25 g. of potassium isocyanide in 5 cc. of water and 50 cc. of methanol. Solution of the ester was complete at the end of two hours, but the mixture stood for forty-eight hours. It was then neutralized with an equivalent of hydrochloric acid, diluted with 50 cc. of ether, and the potassium chloride filtered. The solution was concentrated and the residue fractionated at reduced pressure, yielding (1) 1 g., b. p. 85–100° (2 mm.); (2) 3.9 g. CH(COOMe)=CH-COOH, b. p. 145–155° (2 mm.), m. p. 143°; (3) 2.5 g. of viscous oil, b. p. 190–200° (3 mm.). Fraction I was identified as methoxysuccinic ester, as described below. Fraction 3 was redistilled and boiled at 178–180° (3 mm.).

Anal. Calcd. for $C_{11}H_{15}O_6N$ (XV): C, 51.37; H, 5.83; N, 5.45; OCH_3, 36.19. Found: C, 51.0, 50.83; H, 5.63, 6.03; N, 5.1; OCH_3, 36.86.

Three and four-tenths grams of this compound was heated in a sealed tube at 200° with 10 cc. of concentrated hydrochloric acid for four hours. The resulting solution was evaporated to dryness on the water-bath, and the crystalline residue dissolved in 15 cc. of boiling acetic anhydride, which on cooling deposited an anhydride that melted at 245–248°. This anhydride was dissolved in boiling water, the solution concentrated and the acid allowed to crystallize. This acid melted at 185–188°. These are, therefore, the lower melting butane-1,2,3,4-tetracarboxylic acid and its anhydride, described by v. Auwers and Jacob.[22]

2 - Cyano - 3,4,5 - carbmethoxycyclopentanone (XVII), (a), and Methoxysuccinic Ester.—Fumaric methyl ester (14.4 g.) was added to a suspension of 6.5 g. of potassium isocyanide in 50 cc. of absolute methanol, which stood at room temperature for four days. The undissolved potassium isocyanide was filtered, washed with ether and, when dry, weighed 3.0 g. The filtrate was neutralized with a

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(33) Avery and Upson, *Am. Chem. J.*, **30**, 600 (1902).

solution of dry hydrochloric acid in absolute methanol and the potassium chloride filtered. The solvent was removed at room temperature under reduced pressure, leaving a residue of 16.3 g. This was fractionated into (1) 5.5 g., b. p. 75–85° (2 mm.); and (2) 5.4 g., b. p. 196–205° (2 mm.).

When the same quantities of reagents stood for six days and the mixture was worked up as above, the same weight of isocyanide was recovered. There was a residue of 14.7 g. which was fractionated into (1) 3.0 g. and (2) 6.6 g. The combined low boiling fractions boiled completely at 119° (21 mm.), and was identified as methoxysuccinic ester by saponification to methoxysuccinic acid,[20] m. p. 107–108°. Fraction 2 of both experiments was identified as the cyclopentanone derivative (XVII), obtained also in the following experiment, by its boiling point, brilliant coloration with ferric chloride and complete solubility in sodium bicarbonate solution.

(b).—A solution of 14.4 g. of fumaric methyl ester in 150 cc. of absolute methanol was boiled for two hours with 3.25 g. of potassium isocyanide. The solvent was then removed completely, the gummy residue suspended in ether and shaken with acid until completely dissolved. The residue from the dried ether extract weighed 10.8 g. and boiled at 190–200° (4 mm.). On redistillation it was obtained as a colorless, extremely viscous liquid, b. p. 196° (4 mm.). The substance is completely soluble in sodium bicarbonate solution and is recovered unchanged on acidification of that solution. With ferric chloride it gives a brilliant scarlet coloration.

Anal. Calcd. for $C_{12}H_{13}O_7N$ (XVII): C, 50.89; H, 4.59; N, 4.95; OCH_3, 32.86. Found: C, 50.72; H, 4.67; N, 5.4; OCH_3, 32.08.

Six grams of this viscous liquid was boiled for two hours with 50 cc. of concentrated hydrochloric acid. The solution was evaporated to dryness, leaving a crystalline residue which was absolutely insoluble in organic solvents, nor did it melt below 300°, but charred and sublimed. This was not investigated further, but was boiled with concentrated hydrochloric acid and amyl nitrite. The dark solution was concentrated to about 5 cc., and diluted with 100 cc. of acetone to precipitate any unaltered infusible substance, which was filtered. The filtrate was decolorized with charcoal and concentrated, yielding a crystalline acid, which after recrystallization from acetone–ether melted at 188° with decomposition. This was suspended in ether and treated with excess of diazomethane, giving a clear solution, from which was obtained an ester, crystallizing from petroleum ether in needles, m. p. 63–64°. This fixes the acid as cyclopentanone-3,4-dicarboxylic acid,[23] and establishes the structure of the cyclopentanone derivative (XVII). The infusible compound is undoubtedly an amide sufficiently stable to withstand hydrolysis with acids.

Action of Potassium Isocyanide on Citraconic Methyl Ester, (a), at Room Temperature.—Citraconic methyl ester (15.8 g.) was added to a suspension of 6.5 g. of potassium isocyanide in 50 cc. of absolute methanol, which then stood at room temperature for four days. The undissolved salt, when filtered, washed with ether and dried, weighed 3.5 g. The filtrate was neutralized with a solution of dry methyl alcoholic hydrochloric acid, the potassium chloride filtered, and the solution concentrated to a solvent-free residue of 17.8 g. This was fractionated into (1) 10 g., b. p. 120–135° (20 mm.); and (2) 4.6 g. of viscous liquid, b. p. 167–175° (1 mm.), which solidified on standing.

When the same quantities of reagents were allowed to stand for six days and worked up in the same manner, 2.6 g. of isocyanide was recovered, and 17.2 g. of oil was obtained, which was fractionated into (1) 7 g., and (2) 6.5 g. The solid (fraction 2) was recrystallized from acetone–petroleum ether and ether–petroleum ether and melted at 80–81°.

Anal. Calcd. for $C_7H_9O_4N$, (XIX) or (XX): C, 49.12; H, 5.26; N, 8.19; OCH_3, 18.13; mol. wt., 171. Found: C, 48.87, 48.93; H, 5.32, 5.51; N, 8.34; OCH_3, 17.93; mol. wt. (b. p. of acetone), 173, 174, 178.

The compound is very soluble in water, reacting neutral to litmus and sodium carbonate solution. When boiled with 50% hydrochloric acid, or excess of 20% caustic soda followed by acidification, the solution evaporated to dryness, the resulting acid, extracted from the residue with acetone, was tricarballylic acid, identified by m. p. and mixed m. p. with an authentic sample.

(b), In Boiling Methanol.—Citraconic methyl ester (15.8 g.) was boiled with 6.5 g. of potassium isocyanide in 100 cc. of absolute methanol for four hours, when all the potassium cyanide had dissolved. The solution was cooled and neutralized with dry methyl alcoholic hydrochloric acid. The solution was diluted with ether, the potassium chloride separated by centrifuging, and the solution concentrated at reduced pressure. The residue was distilled at reduced pressure and gave 7.0 g. of $C_7H_9O_4N$, (XIX) or (XX).

1,2-Dicarbmethoxy-3-methoxypropane.—Fraction 1 of the above room temperature reactions was distilled through a Fenske column, and, after removal of a trace of starting material, boiled at 80.5° (1 mm.) and had n^{22}D 1.4294.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.56; H, 7.37. Found: C, 49.88, 50.10; H, 7.20, 7.42.

Saponification of this ester yielded an acid, which, after recrystallization from ether–petroleum ether, melted at 102–103°. Hope[26] gave a m. p. of 92° for $CH_3OCH_2CH(COOH)CH_2COOH$, prepared from the diethyl ester. To check this, the methoxy ester was prepared by an unequivocal procedure. Citraconic methyl ester (15.8 g.) was added to a solution of 0.2 g. of sodium in 50 cc. of absolute methanol and allowed to stand at room temperature for four days. The solution was neutralized and concentrated. The residue was dissolved in ether and a small amount of gelatinous material removed by filtration. The ether-free residue was distilled in a Fenske column and yielded 1.4 g. of starting material and 14.1 g., b. p. 82° (1.5 mm.), n^{22}D 1.4292. and, therefore, identical with the product obtained in the citraconic ester–potassium isocyanide reaction. The acid obtained from this ester melted at 102–103° and did not depress the m. p. of the acid obtained in the previous reaction. Therefore, Hope's acid of m. p. 92° was impure, or the figure given is a typographical error.

Action of Potassium Isocyanide on Benzalacetophenone, $C_{31}H_{25}O_2N$, (XXV).—Benzalacetophenone (10.4 g.) was added to a boiling suspension of 3.3 g. of potassium isocyanide in 50 cc. of absolute methanol. The salt dissolved and, after an hour, a voluminous solid separated. This was filtered from the cooled solution, and when washed colorless with ether and dried it weighed 7.4 g. An additional gram was obtained by concentration of the mother liquor. It is sparingly soluble in all solvents, hot or cold, except hot alcohol and benzene. Recrystallized from the latter solvent, it melted at 237°.

Anal. Calcd. for $C_{31}H_{25}O_2N$ (XXV): C, 83.95; H, 5.64; N, 3.16; mol. wt., 443. Found: C, 84.00; H, 5.75; N, 3.48; mol. wt. (camphor), 418.

In an attempt to oxidize (XXV), 2 g. was added to a solution of 1.1 g. of chromic anhydride in 10 cc. of glacial acetic acid. The mixture was warmed on the water-bath and turned green in about five minutes. The solution was poured into water, and the resulting precipitate separated by filtration. When dry it weighed 1.8 g., and after recrystallization from benzene was identified as $C_{31}H_{23}ON$[27a] by m. p. and mixed m. p. with an authentic sample.

In an attempt to hydrolyze or cleave $C_{31}H_{25}O_2N$ (XXV), 1 g. was treated with a solution of 5 g. of sodium hydroxide in 25 cc. of 50% alcohol at 100° for eighteen hours. The undissolved solid was filtered and dried; weight 0.8 g. After recrystallization, it was identified as $C_{31}H_{23}ON$.

Action of Br_2 on $C_{31}H_{25}O_2N$, (XXV); $C_{31}H_{22}ONBr$.—Five grams of $C_{31}H_{25}O_2N$ (XXV) was suspended in 50 cc. of glacial acetic acid containing 2 g. of bromine. The solution was boiled for ten minutes before the evolution of hydrogen bromide started, but the reaction then proceeded rapidly resulting in a clear pale yellow solution. The cooled solution was poured into water and the precipitated yellow solid separated by filtration. This was dissolved in cold benzene, the water layer drawn off and the benzene dried. Concentration of the benzene solution, and dilution with petroleum ether gave 4.5 g. of colorless solid, which after repeated crystallization from benzene–petroleum ether, melted at 188–189°.

Anal. Calcd. for $C_{31}H_{22}ONBr$: C, 73.81; H, 4.36; Br, 15.85. Found: C, 74.35; H, 4.47; Br, 16.21.

Action of Br_2 on $C_{31}H_{23}ON$.—Eleven grams of $C_{31}H_{23}ON$ was suspended in 100 cc. of glacial acetic acid containing 4 g. of bromine and the mixture boiled. The solid dissolved with evolution of hydrogen bromide and gave a deep red solution. This was poured into water, the water extracted with benzene, which was washed with sodium bicarbonate solution, dried and concentrated, leaving a deep red oil from which no solid could be isolated.

Action of Sodium Methylate on $C_{31}H_{22}ONBr$; $C_{31}H_{21}ON$.—Four grams of $C_{31}H_{22}ONBr$ was suspended in a solution of 0.2 g. of sodium in 50 cc. of absolute methanol and boiled for an hour, during which time the white solid dissolved and a yellow solid crystallized, the solution becoming transitorily pink, and finally yellow. The solution was concentrated to 25 cc., and the solid filtered from the cooled solution; weight, 3.2 g. It crystallized from methanol as lemon-yellow needles, m. p. 188°.

Anal. Calcd. for $C_{31}H_{21}ON$: C, 87.94; H, 4.96. Found: C, 87.41; H, 4.70.

Oxidation of $C_{31}H_{21}ON$, $CH_{24}O_{17}N$.—Two grams of $C_{31}H_{21}ON$ was dissolved in 10 cc. of boiling glacial acetic acid and a solution of 1 g. of chromic anhydride in 5 cc. of glacial acetic acid was added dropwise until the red color was no longer discharged immediately. The solution was poured into water and extracted with benzene, which was washed with water and sodium bicarbonate solution. The acidified sodium bicarbonate solution yielded no solid acid. The dried benzene solution was concentrated and 0.5 g. of white crystalline compound separated. This was recrystallized from benzene and melted at 235–237° with decomposition.

Anal. Calcd. for $C_{24}H_{17}ON$: C, 85.97; H, 5.07. Found: C, 85.93; H, 5.17.

Action of Potassium Isocyanide on Cinnamalmalonic Ester.—Five grams of cinnamalmalonic methyl ester was dissolved in 50 cc. of absolute methanol containing 1.3 g. of potassium isocyanide. The solution stood at room temperature for three hours and was then neutralized with an equivalent of concentrated hydrochloric acid. The precipitated solid was filtered and washed with water, leaving, when dry, 1 g. of white solid. The filtrate was concentrated and yielded an additional 1.5 g. of the same solid. It crystallized from methanol as needles, m. p. 143–144°.

Anal. Calcd. for $C_{29}H_{29}O_8N$: C, 67.05; H, 5.59; N, 2.70; mol. wt., 519. Found: C, 67.35, 67.26; H, 5.76, 5.49; N, 3.5; mol. wt. (boiling acetone), 559, 500, 518.

Action of Potassium Isocyanide on Crotonic Ester.—Twenty grams of crotonic methyl ester was treated with 13 g. of potassium isocyanide in 100 cc. of boiling absolute methanol for forty hours. The dark brown solution was concentrated to 50 cc. and cooled, causing crystallization of 7.0 g. of potassium isocyanide. This was removed by filtration and the filtrate concentrated further. The gummy residue was suspended in ether and shaken with dilute acid until completely decomposed. The dried ether solution was concentrated and the residue fractionated into (1) 4.4 g. of crotonic ester, b. p. 58–70° (25 mm.); (2) 2 g., b. p. 135–145° (4 mm.); and (3) 1.4 g. of viscous liquid, b. p. 190–200° (4 mm.). There was a large tarry residue.

Action of Potassium Isocyanide on Phenylpropiolic Ester, (a) in Absolute Methanol.—Eight grams of phenylpropiolic methyl ester was boiled with a suspension of 6.5 g. of potassium isocyanide in 25 cc. of absolute methanol. The solution turned yellow immediately and, finally, at the end of thirty minutes, dark brown. Since the potassium isocyanide did not seem to be dissolving, the mixture was cooled in an ice-bath and the isocyanide filtered, washed with ether and dried; weight 3.7 g. The filtrate was diluted with 50 cc. of dry ether and neutralized by bubbling in gaseous hydrogen chloride. The potassium chloride was filtered and the filtrate concentrated to a solvent-free residue of 9.9 g. This was fractionated into (1) 6.5 g., b. p. 109–120° (2 mm.), and (2) 2.0 g. of β-cyanobenzylcyanoacetic ester (IX), which distilled when the bath was raised to 240°. Fraction 1 was redistilled and boiled completely at 138–139° (8 mm.). This material gave a ferric chloride test, and, so, 1 g. was treated with excess of saturated cupric acetate solution, thus giving 0.3 g. of a copper derivative that was identified as that of benzoylacetic methyl ester by m. p. (200°) and mixed m. p. The distillate had n^{25}_{D} 1.5455; v. Auwers[34] gives

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[34] Von Auwers, *Ann.*, **413**, 274 (1916); **415**, 230 (1918).

the indices of refraction ($n^{25}D$) of benzoylacetic methyl ester and β-methoxycinnamic methyl ester, respectively, as 1.537 and 1.550. Thus the yield of copper derivative shows a benzoylacetic ester content of 30%, while the index of refraction checks this approximation with benzoylacetic ester content of 35%.

(b). **In Aqueous Methanol.**—Eight grams of phenylpropiolic methyl ester was added to a solution of 6.5 g. of potassium isocyanide in 10 cc. of water and 50 cc. of methanol and allowed to stand at room temperature for four hours and, then, for an additional twenty hours in a bath at −20°. One gram of crystallized potassium salt was filtered and the solution was diluted with 500 cc. of ether, yielding an additional 5.8 g. of potassium salt. The combined potassium salts was suspended in ether and shaken with dilute acid. The dried ether solution yielded 3.5 g. of phenylpropiolic acid. The filtrate from the salt was shaken with dilute acid, changing from deep orange to pale yellow. The dried ether solution was concentrated and left 5 g. of solid, which was extracted repeatedly with petroleum ether, thus leaving 4 g. of pure β-cyanobenzylcyanoacetic ester (IX). The petroleum ether extracts yielded 1 g. of phenyl propiolic acid.

Summary

1. The formation of pyrotartaric dinitrile from potassium isocyanide and allyl cyanide proceeds primarily through rearrangement of allyl cyanide to crotononitrile.

2. The mechanisms hitherto proposed for the syntheses of β-cyano-ketones, -esters and -nitriles from the corresponding α,β-Δ-ketones, -esters and -nitriles, which was assumed to proceed by addition of hydrocyanic acid or through a complex salt with potassium isocyanide to the Δ-carbons of the Δ-compounds has been shown to be impossible.

3. The formation of β-cyano-ketones, -esters and -nitriles from the corresponding α,β-ethylenic compounds proceeds through the formation of enolates, or iminolates, by 1,4-addition of potassium isocyanide to the conjugated groups of the unsaturated compounds, the metal uniting with carbonyl oxygen or cyano nitrogen.

4. When the reaction products from potassium isocyanide and the α,β,Δ-esters are poorly neutralized enolates, in the absence of water, they realize a better intramolecular neutralization by addition to unchanged ester.

5. The action of potassium isocyanide upon fumaric methyl ester proceeds primarily by 1,4-addition; under certain conditions, the enolate adds to unchanged fumaric ester and the addition product condenses to a cyclopentanone derivative. With citraconic methyl ester, the first phase consists in rearrangement to the itaconic ester, which undergoes the 1,4-addition with the isocyanide and is then changed to a cyclic nitrogen derivative.

6. According to the experimental conditions, phenylpropiolic ester unites by 1,4-addition with one and then with a second molecule of isocyanide. The first addition product is an enolate of the structure $C_6H_5C(CN){=}C{=}C(OK)OMe$; a type of enolate involving the enolization of an unsaturated α-CH group of an α,β,Δ-ester.

CAMBRIDGE, MASS. RECEIVED JANUARY 9, 1937

[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Catalytic Hydrogenation and Esterification of C_4-Saccharinic Acid Lactones and the Hydrogenation of Butyl Erythronate[1]

BY J. W. E. GLATTFELD AND ANNE M. STACK

Various reduction methods have been studied in these Laboratories with the object of finding a practical method for the reduction of the C_4-saccharinic acids to the corresponding aldehydes and alcohols and for the reduction of erythronic lactone to erythrose. Low pressure catalytic reduction of aldonic acids was studied by Glattfeld and Shaver[2] and by Glattfeld and Schimpff.[3] The work reported in this paper is a continuation of these experiments and includes a study of the catalytic hydrogenation, under pressures of 2–136 atmospheres, of 2,3-dihydroxybutyric acid lactone and one of its derivatives, of 1,3-dihydroxybutyric acid lactone, and of the butyl ester of *dl*-erythronic acid. The last named compound was first prepared in these Laboratories by Snoddy.[4] His method of preparation was followed in general but, as a few changes were made, the procedure is given in some detail in the Experimental Part. (Hereinafter the 2,3- and 1,3-dihydroxybutyric

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[1] This article is condensed from a dissertation which will be presented by Anne M. Stack in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

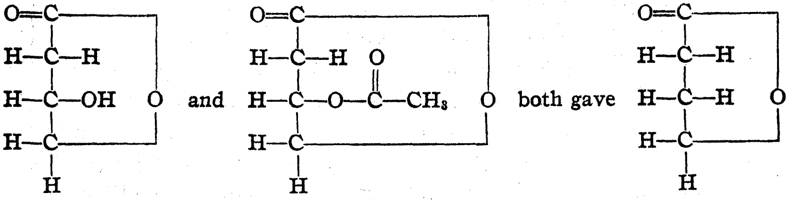
[2] Glattfeld and Shaver, THIS JOURNAL, **49**, 2305 (1927).

[3] Glattfeld and Schimpff, *ibid.*, **57**, 2204 (1935).

[4] J. A. Snoddy, S.M. Dissertation, University of Chicago, 1934.

acid lactones will be called, respectively, the 2,3- and 1,3-acid lactones, and the *dl*-butylerythronate, the butyl ester.)

Attempts to reduce the 2,3-acid lactone at low pressures (2–3 atmospheres), with small amounts of catalyst were at first unsuccessful. When the rate of shaking was tripled[3] and the amount of catalyst greatly increased, a 21% reduction of the 2,3-acid lactone and a 67% reduction of the 1,3-acid lactone (products not isolated) were effected. At high pressures (119–133 atmospheres), 37–65% reductions of the 2,3-acid lactone and a 54% reduction of the acetyl-2,3-acid lactone were obtained: the main product was 3-hydroxybutyric acid lactone.

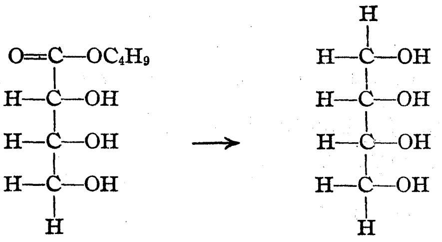


2,3-Acid lactone

Acetyl-2,3-acid lactone

3-Hydroxybutyric acid lactone

The 1,3-acid lactone and the 2,3-acid amide yielded no definite results. A few experiments on the high pressure reduction of erythronic lactone and of erythronamide gave no definite results. The butyl ester was then prepared and reduced to erythritol in good yield under both low and high pressures.



The butyl ester

Erythritol

Further work on catalytic hydrogenation in this field is in progress.

Experimental Part

Apparatus.—The apparatus used for pressures up to three atmospheres was that made by the Burgess–Parr Company of Moline, Illinois. In the work at higher pressures, two different bombs made in the Chemistry Department shop were used. One of these (Bomb A), was essentially the bomb described by Peters and Stanger.[5] We used a glass container with a pin-hole opening inside this bomb. The other bomb (Bomb B) was similar to the one made by the American Instrument Company and diagramed by Tongue.[6] The inside of this bomb was first tinned and then silvered. For valuable help in connection with the construction and testing of these bombs, we wish to thank Dr. F. N. Peters, Jr., and Mr. J. Pokorny of the Quaker Oats Company, Dr. C. W. Lenth of the Miner Laboratories, and the Crane Company of Chicago.

Materials.—(1) The 1,3- and 2,3-acid lactones were prepared according to the procedures developed in these Laboratories and published in previous articles.[7] The crude lactones were twice fractionated and then had the boiling ranges, 110–112° at 2–4 mm., and 148–150° at 2–4 mm., respectively. They were faintly yellow mobile liquids. (2) The acetyl-2,3-acid lactone has been prepared[8] in 52.7% yield by the addition of the 2,3-acid lactone to a cooled (0°) mixture of acetic anhydride and freshly fused zinc chloride. Our product was prepared by the interaction of the sodium salt of the 2,3-acid with acetyl chloride (see below). (3) The *dl*-erythronic lactone was prepared according to the method of Braun.[9] It was a perfectly white crystalline material, m. p. 91–92°. (4) Platinic oxide monohydrate (in the quantities recommended by Schimpff[8]) and palladium oxide were prepared by the procedure of Adams, Voorhees and Shriner.[10] (5) The copper–chromium oxide catalyst was prepared according to Adkins and Connor.[11] (6) The copper–barium–chromium oxide catalyst (37 KAF), was prepared by the method of Connor, Folkers and Adkins.[12] (7) The "Raney" (Ni) catalyst was kindly supplied by the Quaker Oats Company. It had been prepared by the procedure of Covert and Adkins.[13]

Preparation of Acetyl-2,3-acid Lactone.—The sodium salt of the 2,3-acid was prepared by the titration of a heated 10% aqueous solution of the 2,3-acid lactone with a 0.5 N solution of sodium hydroxide. The resulting solution was concentrated to dryness at reduced pressure and the sodium salt obtained in the form of a light brown gum. Six equivalents of acetyl chloride was added to each of a 77 and 79-g. batch of sodium salt. The mixtures were refluxed in a water-bath at 50–60° for four hours and at 60–85° for two hours, at the end of which time all of the sodium salt had disappeared. The solutions were combined, the sodium chloride was separated by filtration and washed with glacial acetic acid and the combined mother liquor and washings concentrated to dryness at reduced pressure at 60°. The residue was fractionated in two batches since it had previously been noted that long continued heating results in some decomposition. A large fraction distilled over at 119–121°, 4 mm. At 121° some

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(5) Peters and Stanger, *Ind. Eng. Chem.*, **20**, 74 (1928).

(6) H. F. Tongue, "The Design and Construction of High Pressure Chemical Plant," Chapman and Hall, Ltd., London, 1934, p. 289.

(7) (a) Glattfeld and Sander, THIS JOURNAL, **43**, 2675 (1921); (b) Glattfeld, Leavell, Spieth and Hutton, *ibid.*, **53**, 3164 (1931).

(8) C. E. Ford, S.M. Dissertation, University of Chicago, 1932.

(9) Braun, THIS JOURNAL, **51**, 235 (1929).

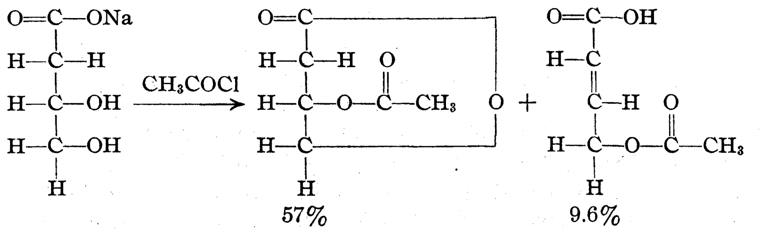
(10) Adams, Voorhees and Shriner, "Organic Syntheses," Vol. VIII, John Wiley and Sons, Inc., New York City, 1928, p. 92.

(11) Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

(12) Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

(13) Covert and Adkins, *ibid.*, **54**, 4116 (1932).

fuming was noted; at 133° crystals appeared in the condenser: a mixture of solid and oil distilled at 133–140°, 4.5 mm. The 119–121° fraction was redistilled to give 90 g. of boiling range 119–121°, 4 mm., a 57% yield of acetyl-2,3-acid lactone. The solid was separated by filtration from the high boiling oil which came over with it, and dried on a porous plate to give 19.5 g. of crude material. This was recrystallized from a small amount of hot ethyl acetate and dried to give 15.3 g. of white crystalline material, melting range 99–102°. It was distilled under reduced pressure for further purification: the distilled solid had the same melting range. This compound, obtained in 9.6% yield, may be the *trans*-3-acetyl crotonic acid, melting point 97–98°, reported by Rambeau.[14]



Anal. Calcd. for $C_6H_8O_4$: C, 49.99; H, 5.60. Found: (liquid, 119–121°, 4 mm.) C, 49.85, 49.98; H, 5.56, 5.53; (solid, m. p. 99–102°) C, 49.92, 50.22; H, 6.27, 5.74.

Neutralization equivalent. Calcd. for $C_6H_8O_4$, 72. Found: liquid, 74.2 and 74.6 (0.2184, 0.2333 g. required 29.44 and 31.28 cc. 0.1 *N* alkali); solid, 72.1 and 72.0 (0.1841, 0.2059 g. required 25.55 and 28.60 cc. 0.1 *N* alkali).

Results of Reduction Experiments.—The results obtained and the conditions used in some representative experiments are recorded in the tables. A few experiments will be discussed in detail to illustrate the experimental procedures used.

Reduction of Lactones

High Pressure Reduction of 2,3-Acid Lactone (Expt. No. 5 in Table I).—Fifty grams of 2,3-acid lactone was put into the glass container of Bomb A and 6.2 g. of copper–barium–chromium oxide catalyst (37 KAF) added. The air was displaced and the bomb placed on two electric heaters mounted in a shell which rocked at the rate of 42 cycles per minute. The material was put under pressure of 88 atmospheres of hydrogen and heating started. After one hour the temperature had reached 167° and the pressure 129 atmospheres, and, after another half hour, 182° and 125 atmospheres. The temperature remained at 182° for three and seven-tenth hours and the pressure continued to drop as hydrogen was used. Heating was then discontinued but the bomb was allowed to rock under pressure for two more hours. At the end of this time the bomb had cooled to 74° and the pressure, 77 atmospheres, could be released without loss of material. The liquid was filtered and fractionated at reduced pressure. The first fractionation yielded 24 g. of material of boiling range 76–78° at 5 mm. This was refractionated at atmospheric pressure and yielded 21.4 g. of material of boiling range 199–202°, 50.8% calculated as 3-hydroxybutyric acid lactone.

The liquid was identified as 3-hydroxybutyric acid lactone by its neutralization equivalent and by oxidation to succinic acid.

Anal. Subs., 0.2038, 0.2613 g.: 0.1 *N* alkali 23.65, 30.39 cc. Neutralization equivalent calcd. for $C_4H_6O_2$, 86.0. Found: 86.2, 86.0.

Conversion to Succinic Acid.—Ten grams of chromic anhydride was made up to 70 cc. with water and 6 cc. of concentrated sulfuric acid. Five grams of the liquid was mixed with 54.3 cc. of this solution, which volume contained 7.75 g. of chromic anhydride, the amount necessary for this oxidation. The mixture was refluxed for one and one-half hours until the original yellow color had changed to green, extracted four times with ether using 150 cc. for each extraction, and the ether extract concentrated at reduced pressure at 60°. The white residue, dried over sulfuric acid, weighed 3.0 g. After two recrystallizations from water 0.6 g. of white crystalline material, melting range 182–184°, 8.7% calculated as succinic acid, was obtained. No attempt was made to rework the mother liquor.

Anal. Subs., 0.2275, 0.2488 g.: 0.1 *N* alkali 38.08, 41.64 cc. Neutralization equivalent calcd. for $C_4H_6O_4$, 59. Found: 59.7, 59.8.

High Pressure Reduction of Acetyl-2,3-acid Lactone (Expt. No. 8 in Table I).—Fifty grams of acetyl-2,3-acid lactone was put into the glass container of Bomb A and 0.4 g. of platinic oxide monohydrate added. The air was displaced, the material was put under pressure of 97 atmospheres of hydrogen, rocked at the rate of 42 cycles per minute, and heating begun. In one hour the temperature had reached 158° and the pressure 129 atmospheres. The temperature remained between 161 and 142° for the next 20.1 hours at the end of which time the pressure had dropped to 82 atmospheres. Heating was stopped but rocking continued. The pressure was released 4.4 hours later when the temperature of the bomb was 31°. The glass container had leaked at the stopper and the bomb now contained only 37.6 g. of filtered material. The liquid, fractionated at reduced pressure, yielded 24.9 g. of material, boiling range 20–68°, 5 mm. On redistillation at atmospheric pressure, 12.2 g. of material, boiling range 195–203°, was obtained. This is a yield of 54.3% calculated as 3-hydroxybutyric acid lactone on the basis of 37.6 g. of original material.

Anal. Subs., 0.2014 g.: 0.1 *N* alkali 23.33 cc. Neutralization equivalent calcd. for $C_4H_6O_2$, 86.0. Found: 86.3.

Alkalinity Developed by $PtO_2 \cdot H_2O$.—Certain results, obtained in the analysis of samples from low pressure reduction experiments, indicated that the acid was being neutralized very slowly during the reduction. That the catalyst was responsible for this was shown by the experiment outlined below.

A 2-g. sample of the catalyst was added to 50 cc. of water and the mixture shaken under pressure of 2.8 atmospheres

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[14] Rambeau, *Bull. soc. chim.*, [5] **1**, 1317 (1934).

TABLE I

HIGH PRESSURE REDUCTION[a] OF THE 2,3-ACID LACTONE, THE ACETYL-2,3-ACID LACTONE AND THE 1,3-ACID LACTONE

Expt.	Lactone	Amt., g.	Vol. aq. soln., cc.	Catalyst	Cat., g.	Max. press., atm.	Range of max. temp., °C.	Time of hyd. over range of max. temp., hrs.	Total time of hyd., hrs.	% yield of 3-hydroxy-butyric acid lactone,	
										Isolated	Corr.[b]
1	2,3-Acid	20	95	$PtO_2 \cdot H_2O$	0.2	126	158–167	5.9	7.9	23.7	46.9
2	2,3-Acid	20	60	$PtO_2 \cdot H_2O$	.2	133	182–189	5.9	10.8	31.4	65.4
3	2,3-Acid	49	25	Cu–Cr oxide	6.0	119	150–159	1.8	6.1	26.6	39.2
4	2,3-Acid	50	..[c]	PdO	0.4	127	171–182	4.5	8.9	37.2	
5	2,3-Acid	50	..	Cu–Ba–Cr oxide (37 KAF)	6.2	129	182	3.7	7.2	50.8	
6	2,3-Acid	50	..	Cu–Cr oxide	6.0	57	211–242	3.1	11.9	19.0	
7	2,3-Acid	50	..	"Raney"	13.0 (moist)	129	169–173	8.1	11.0	48.7	54.3
8	Acetyl-2,3-acid	50	..	$PtO_2 \cdot H_2O$	0.4	129	142–161	20.1	25.5	54.3	
			Solv. vol., cc.								
9	1,3-Acid	20	25, 95% alc.	$PtO_2 \cdot H_2O$	0.4	112	146–176	16.6	22.7	..	
10	1,3-Acid	20	20 water	$PtO_2 \cdot H_2O$	.4	128	156–168	26.1	27.2	..	
11	1,3-Acid	20	20 water	"Raney"	8.0 (moist)	115	145–161	19.0	22.2	..	
12	1,3-Acid	20	20 water	Cu–Ba–Cr oxide (37 KAF)	3.0	136	154–181	25.8	26.8	..	

[a] The rate of rocking was 42 cycles per minute. [b] 3-Hydroxybutyric acid lactone distils with steam. The distillate was saved and titrated for acidity. Consideration of this factor gave a corrected yield. [c] No solvent was used in Experiments 4–8.

of hydrogen for three-tenths hour. A 1-cc. sample now required 2.49 cc. of 0.01 *N* acid for neutralization. The 49 cc. of solution was again shaken under pressure of 2.8 atmospheres of hydrogen for four-tenths hour. A 1-cc. sample now required 2.60 cc. of 0.01 *N* acid, showing practically no increase in alkalinity during the second period of hydrogenation. A further 2 g. of catalyst was added to the 48 cc. of solution which remained. The mixture was again shaken under pressure of 2.8 atmospheres of hydrogen for one-half hour. A 1-cc. sample now required 5.28 cc. of 0.01 *N* acid, indicating that the second 2 g. of catalyst had generated an alkalinity equivalent to 2.68 cc. of 0.01 *N* acid. From a consideration of these data and others, it was concluded that an average alkalinity equivalent to 2.55 cc. of 0.01 *N* acid was generated by the introduction of 2 g. of the catalyst used in the reduction of the 2,3-acid lactone. The corresponding correction factor on the particular lot of catalyst used in the reduction of the 1,3-acid lactone was found to be 3.26 cc.

These facts and the further fact that water, shaken up with a sample of the catalyst, gave no test for nitrates before reduction, yet gave a test for ammonia after reduction, indicated that the alkalinity developed was due to the formation of ammonia by the reduction of oxides of nitrogen occluded by the catalyst.

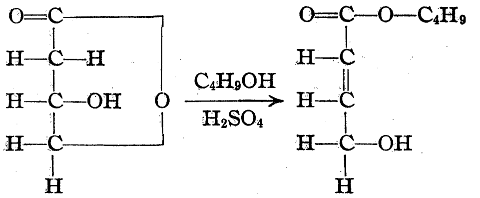
Low Pressure Reduction of 2,3-Acid Lactone.—A 5.06 g. sample of 2,3-acid lactone was dissolved in water, made up to a volume of 100 cc., 2 g. of platinum catalyst added and the solution hydrogenated in the Burgess–Parr apparatus under 2.9 atmospheres of hydrogen for two and six-tenths hours with shaking at the rate of 360 cycles per minute. A 1-cc. sample required 47.11 cc. of 0.01 *N* alkali for neutralization. (This includes the correction introduced because of alkalinity generated by the catalyst.) A 1-cc. sample of the original solution was neutralized by 49.63 cc. of 0.01 *N* alkali. A 5.1% reduction had therefore occurred. Periodic addition of a total of 16 g. of catalyst over a period of 12.4 hours effected a reduction of only 21.4%.

Low Pressure Reduction of 1,3-Acid Lactone.—A 5.06-g. sample of 1,3-acid lactone was dissolved in water and made up to a 50-cc. volume. The procedure was identical with that of the preceding experiment. A 67.3% reduction was effected after the addition of 12 g. of platinum catalyst, in portions, over a period of 36.9 hours.

Attempts to Prepare Esters of C_4-Saccharinic Acids

The direct reduction of the 2,3- and 1,3-acid lactones to the corresponding alcohols not having proved feasible, it was decided to attempt to reduce esters of the acids in the hope that these might be more susceptible to the type of reduction sought. In spite of many trials none of the desired esters could be prepared. The results of some of the experiments, however, may be worthy of record.

Butyl 3-Hydroxyisocrotonate from 2,3-Acid Lactone.—Fifty-one grams of 2,3-acid lactone was dissolved in 112 cc. of absolute butanol, 1.4 cc. of concentrated sulfuric acid added, and the solution refluxed for ten hours. It was concentrated to dryness at reduced pressure, finally at 50°, to give an 88.7-g. residue. Five grams of calcium carbonate and 50 cc. of water were added to the residue and the mixture was concentrated to dryness at reduced pressure finally at 68°. The residue was extracted and the salts were washed thoroughly with ether. The ether



2,3-Acid lactone

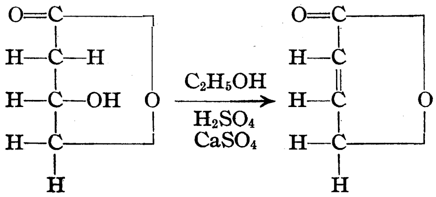
Butyl-3-hydroxy-isocrotonate

extract was dried over anhydrous sodium sulfate and concentrated at atmospheric pressure to give 72 g. of crude residue which, on fractionation, gave 40.2 g. of water-insoluble liquid, boiling range 179–183° (3 mm.), a 50.9% yield calculated as butyl 3-hydroxyisocrotonate. In another experiment in which 102 g. of lactone was treated according to the same procedure, a 75.5-g. sample, 47.8% yield, boiling range 174–181° (2 mm.) was obtained.

Anal. Subs. 0.2701, 0.3089 g.: 0.1 *N* alkali 17.07, 19.64 cc. Neutralization equivalent calcd. for $C_8H_{14}O_3$, 158.1. Found: 158.2, 157.3.

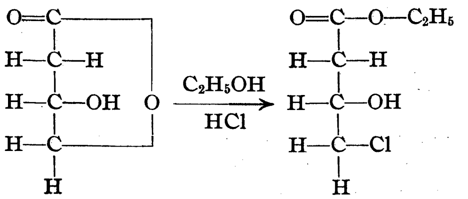
3-Hydroxyisocrotonic Lactone from 2,3-Acid Lactone.—Two hundred and five grams of 2,3-acid lactone was dissolved in 1040 cc. of absolute ethanol, four drops of concentrated sulfuric acid and 100 g. of anhydrous calcium sulfate added, and the mixture refluxed for seventy-five and seven-tenths hours. The solution was filtered and the alcohol was distilled off at reduced pressure to give a 235 g. residue which was dissolved in water. The solution was neutralized with sodium bicarbonate and the water distilled off at reduced pressure, finally at 60°. The residue was dissolved in ether and the ether solution dried over anhydrous sodium sulfate. The ether was distilled off at atmospheric pressure and the residue fractionated to give 99.6 g. of material, boiling point 76–77° (3.5 mm.), m. p. 5°, a 59% yield calculated as 3-hydroxyisocrotonic lactone. The titration results varied due probably to some structural change which the lactone undergoes in hot solution.[7b]

Under the conditions of this experiment, the lactone was simply dehydrated.



2,3-Acid lactone 3-Hydroxyisocrotonic lactone

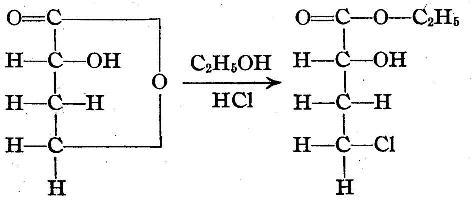
Ethyl 2-Hydroxy-3-chlorobutyrate[15] from 2,3-Acid Lactone.—Ten grams of 2,3-acid lactone was dissolved in 100 cc. of absolute ethanol, the solution was cooled in an ice-bath, and dry hydrogen chloride was passed in to saturation (one and one-half hours). After twelve hours in the ice box, the alcohol was removed by vacuum distillation and the 14 g. of residue was extracted with ether. The ether solution was dried over anhydrous sodium sulfate, the ether distilled off, the residue fractionated, and 7.0 g. of material of boiling range 92–95° (4 mm.), a 42.9% yield calculated as ethyl 2-hydroxy-3-chlorobutyrate, was obtained. Experiments were performed in which the volume of the alcohol varied from five to fifty times that of the lactone: the chief product was always ethyl 2-hydroxy-3-chlorobutyrate.



2,3-Acid lactone Ethyl 2-hydroxy-3-chlorobutyrate

Anal. Subs., 0.2972, 0.3422, 0.2623 g.: 0.1 *N* alkali 35.40, 40.79 cc.; 0.1 *N* silver nitrate 15.43 cc. Calcd. for $C_4H_{11}O_3Cl$: neutralization equivalent, 83.2; Cl, 21.31. Found: neutralization equivalent 84.0, 83.9; Cl, 20.86.

Ethyl 1-Hydroxy-3-chlorobutyrate from 1,3-Acid Lactone.—Fifty-one grams of 1,3-acid lactone was dissolved in 500 cc. of absolute ethanol, the solution was cooled in an ice-bath, and dry hydrogen chloride passed in to saturation (eight and three-tenths hours). The alcohol was distilled from the solution at reduced pressure and 71.6 g. of residue obtained. Water was added and the hydrochloric acid neutralized with sodium bicarbonate. The neutral mixture (two layers) was concentrated to dryness with a water pump finally at a bath temperature of 50°. The residue was extracted with absolute ethanol, the sodium chloride separated by suction filtration, and the filtrate concentrated to dryness with a water pump, finally at 50°, to give a 63.6-g. residue. The residue was shaken with 100 cc. of water, the layers separated, the 43 g. of water-insoluble material dissolved in 220 cc. of ether, and the solution dried over anhydrous sodium sulfate. Removal of the ether and fractionation of the 38.6 g. of residue gave 28.2 g. of material, boiling range 84–87°, 1.5 mm. Refractionation gave 27 g. of material, 92–95°, 1.5 mm., a 32.5% yield calculated as ethyl 1-hydroxy-3-chlorobutyrate.



1,3-Acid lactone Ethyl 1-hydroxy-3-chlorobutyrate

Anal. Subs., 0.2908, 0.2913, 0.2756, 0.2850 g.: 0.1 *N* alkali 34.22, 34.40 cc.; 0.1 *N* silver nitrate 16.04, 16.64 cc. Calcd. for $C_4H_{11}O_3Cl$: neutralization equivalent, 83.2; Cl, 21.31. Found: neutralization equivalent, 85.0, 84.7; Cl, 20.64, 20.70.

Reduction of Butyl Erythronate

Preparation of Butyl Erythronate.—This compound was made by a modification of Snoddy's adaptation of a special method of preparation of the esters of aldonic acids.[16] The necessary calcium erythronate was prepared in 87% yield by the treatment of a water solution of erythronic lactone with calcium carbonate at 90° followed by concentration of the filtered solution at reduced pressure and addition of absolute ethanol to precipitate the salt.

Eighty grams of calcium erythronate, dried to constant weight in an air oven at 95°, was mixed with 288 cc. of absolute butanol in a three-necked tube fitted with a mercury-seal stirrer and inlet and outlet tubes for hydrogen chloride. As dry hydrogen chloride was passed into the suspension, the salt dissolved. In forty-five minutes the

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(15) G. Braun, THIS JOURNAL, **52**, 3167 (1930).

(16) Hlasiwetz and Habermann, *Ann.*, **155**, 127 (1870); Herzfeld, *ibid.*, **244**, 294 (1888); Kohn, *Monatsh.*, **16**, 333 (1895).

temperature of the cloudy solution was 61°. At the end of two hours a heavy precipitate was present but the stream of hydrogen chloride was allowed to run during another forty minutes. The mixture of sirup and precipitate was transferred from the tube to a beaker by means of dry ether and stored in a desiccator over calcium chloride. When the fine white precipitate had settled the ether was decanted, fresh ether added and the solid again allowed to settle out in the desiccator. This process, which was repeated a third time, removed the butanol and some of the hydrogen chloride. The white solid $[(C_3H_7O_3COOC_4H_9)_2\cdot CaCl_2]$ was very hygroscopic. It was separated quickly from the ether by suction filtration, washed several times with dry ether, and stored over calcium chloride in a desiccator which was evacuated continuously until all of the ether was removed. Dry air was then drawn through the desiccator until all of the hydrogen chloride had been removed. At this point the salt was added to a similar lot obtained in a previous run from 53 g. of calcium erythronate. The weight of the material from the combined runs was 179 g., a 73.3% yield based on erythronic lactone.

The dried solid was dissolved in a very small amount of water and treated with a little silver oxide to remove residual hydrogen chloride. The procedure from this point on was that of Hlasiwetz and Habermann. A slight excess of sodium sulfate in water solution was added and the calcium sulfate separated by suction filtration. The filtrate was concentrated to dryness at reduced pressure with the bath finally at 50°. The residue was extracted with ether and the ether solution concentrated at reduced pressure until it appeared cloudy. It was then cooled, the solid separated by suction filtration and washed with a little dry ether. The washings and mother liquor were further concentrated and cooled to give more solid. The solid, after drying in a vacuum desiccator over calcium chloride, weighed 102 g. and melted at 62–64°, a 53.9% yield based on erythronic lactone.

Anal. Subs., 0.2962, 0.3156 g.: 0.1 *N* alkali 15.50, 16.42 cc. Neutralization equivalent calcd. for $C_8H_{16}O_5$, 192.1. Found: 191.1, 192.2. A fairly satisfactory analysis for C and H has been reported already by Snoddy.

Butyl erythronate is a glistening white odorless compound, is decidedly "greasy" to the touch, and is very soluble in alcohol, acetone and water. It may be crystallized from ether.

High Pressure Reduction (Expt. No. 1, Table II).—Thirty grams of butyl erythronate was dissolved in 156 cc. of 95% ethanol (solution volume, 179 cc.). A 2-cc. sample was removed for analysis and the remainder of the solution was put into Bomb B. Five grams of platinum oxide catalyst was added, the air was displaced, and the material put under pressure of 97 atmospheres of hydrogen and rocked at the rate of 42 cycles per minute. After 25.6 hours the bomb was opened and a 2-cc. sample removed for analysis. A 53.25 cc. volume of 0.1 *N* sodium hydroxide was added to the sample and the solution was refluxed for 0.75 hour to ensure complete hydrolysis of the ester. Titration with 0.1 *N* hydrochloric acid showed that the sample had neutralized 11.29 cc. of 0.1 *N* alkali. Since a 2-cc. sample of solution before reduction required 18.44 cc. of 0.1 *N* alkali, a 38.8% reduction had been accomplished. Three grams of catalyst was added to the remaining solution which was put under pressure of 95 atmospheres of hydrogen and the above procedure carried out again. This process was continued until a complete reduction of the ester was effected. This required a period of 114.1 hours and the addition, in portions, of 20 g. of catalyst. Erythritol was isolated in 60.1% yield.

Low Pressure Reduction (Expt. No. 2, Table II).—Thirty grams of butyl erythronate was dissolved in 151 cc. of 95% ethanol. A 2-cc. sample was removed, the remaining solution was put into a pressure bottle, 1 g. of platinum oxide catalyst added, the bottle evacuated, and the material put under pressure of 2–3 atmospheres of hydrogen. The procedure for removal of sample, analysis, addition of more catalyst, etc., was identical with that used in the high pressure experiment. Complete reduction of the ester was effected in 329.5 hours by the addition, in portions, of 14.7 g. of catalyst. Erythritol was isolated in 68.5% yield.

TABLE II

REDUCTION OF BUTYL ERYTHRONATE

Sample, 2 cc.	$PtO_2\cdot H_2O$, g.	Time of hyd., hrs.	0.1 *N* NaOH, cc.	Ester, %	Reduction, %	Erythritol isolated, %
Expt. 1[a]: 30 g. of butyl erythronate in 156 cc. 95% alc.						
Orig.	..	...	18.44	100.0	0.0	
A	5	25.6	11.29	61.2	38.8	
B	3	21.9	7.54	40.9	59.1	
C	3	13.9	4.61	25.0	75.0	
D	5	25.2	1.44	7.8	92.2	
E	4	27.5	0.00	0.0	100.0	
Summary	20	114.1				60.1
Expt. 2[b]: 30 g. of butyl erythronate in 151 cc. 95% alc.						
Orig.	..	...	18.19	100.0	0.0	
A	1	2.9	17.96	98.7	1.3	
B	1	18.5	16.42	90.3	9.7	
C	1	27.5	14.74	81.0	19.0	
D[c]	0.5	21.1	13.71	75.4	24.6	
E	.5	2.8	13.14	72.2	27.8	
F	.5	20.0	12.14	66.7	33.3	
G	2.0	23.5	8.86	48.7	51.3	
H	2.0	24.3	5.68	31.2	68.8	
I	2.0	40.7	2.13	11.7	88.3	
J	3.0	18.1	1.30	7.1	92.9	
K	0.6	20.3	0.73	4.0	96.0	
L	..[d]	67.5	.54	3.0	97.0	
M	0.6	42.3	.00	0.0	100.0	
Summary	14.7	329.5				68.5

[a] Rate of shaking, 42 cycles per minute; pressure 82–97 atm. [b] Rate of shaking, 360 cycles per minute; pressure 2–3 atm. [c] Crystals of erythritol on sides of pressure bottle. [d] Aerated, 3.3 hours.

Isolation of Erythritol.—The details of the isolation of erythritol from the reported high pressure run will be given. The solution, analysis of which indicated complete reduction of the ester, was separated from the catalyst by suction filtration. The catalyst was washed with water and the combined washings and mother liquor were subjected to distillation to dryness at reduced pressure to give 19.1 g. of residue. The residue was dissolved in a small amount of water, the solution heated with charcoal to 100°, the charcoal removed and the solution again subjected to distillation to dryness at reduced pressure to give 18.7 g. of residue. Several recrystallizations from 95% alcohol gave successively 8.0 g. of crystals, m. p. 119–121.5°; 2.5 g., m. p. 118–121°; and 0.2 g., m. p. 118–120.5°; a total yield of 10.7 g. The total volume of solution in the reported high pressure experiment was 179 cc., but since 12 cc. of this solution had been used for analyses, the maximum possible yield was 17.8 g. Erythritol was therefore isolated in 60.1% yield.

Summary

1. The method of catalytic hydrogenation at high pressures has been applied to two C_4-saccharinic acid lactones and to erythronic lactone.

2. Both the 2,3-dihydroxybutyric acid lactone and its 2-acetylated derivative have been reduced in good yield to 3-hydroxybutyric acid lactone.

3. The 2,3-dihydroxybutyric acid lactone and the 1,3-dihydroxybutyric acid lactone showed, respectively, by analyses, 21 and 67% reduction at low pressures when large amounts of platinum oxide catalyst were used.

4. Butyl erythronate was prepared according to a modification of Snoddy's adaptation of the method of Hlasiwetz and Habermann. It was reduced to erythritol in good yield at both high and low pressures.

5. The butyl ester of 3-hydroxyisocrotonic acid and the ethyl ester of 1-hydroxy-3-chlorobutyric acid have been prepared.

6. The esters mentioned in 4 and 5 above are new to the literature.

7. Reduction of samples of the catalyst ($PtO_2 \cdot H_2O$) resulted in the production of a slight amount of alkali. This fact should not be ignored in hydrogenations of acids, esters, etc.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 8, 1937

NOTES

The Action of the Sulfonyl Group

BY F. ARNDT

In a recent paper[1] Kohler and Potter, after giving reference to a previous work of Arndt and Martius,[2] and after describing the behavior of a series of sulfonyl ketones, conclude as follows: "The view that sulfonyl groups cannot promote enolization is manifestly no longer tenable." This view, however, has not been expressed by the writer and his co-workers, who have even given detailed experimental evidence to the contrary. Thus, malonic ester does not enolize, whereas tosylmalonic ester enolizes appreciably; malonitrile does not tautomerize, but tosylmalonitrile tautomerizes considerably; acetaldehyde and tosylacetaldehyde do not enolize whereas formyl methionide, where the aldehyde group is combined with *two* sulfonyl groups in the β-position, enolizes to a great extent. On the other hand, Kohler and Potter acknowledge that "it is doubtless true that the sulfonyl group is far less effective than the carbonyl group in promoting enolization." This great difference in *degree* has been attributed by Arndt and Martius to a difference in the *nature* of the action of the sulfonyl and carbonyl groups, respectively. The action of the sulfonyl group is purely acidifying, thereby diminishing the factor which is opposed to enolization, *i. e.*, the "prototropic expenditure of work," whereas carbonyl and other groups containing multiple bonds increase, to a great extent, the active factor which promotes enolization, *i. e.*, the "electromeric effect of the molecule," by forming with the enolic double bond a conjugated system. The view that the sulfonyl group does not act in *this* manner, because it does not contain double bonds, is in no way contradicted by the experimental results of Kohler and Potter. The behavior of the group $COC_6H_2(CH_3)_3$ alone and in combination with one or two sulfonyl groups is, in fact,

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[1] E. P. Kohler and H. A. Potter, THIS JOURNAL, **58**, 2166 (1936).

[2] F. Arndt and C. Martius, *Ann.*, **499**, 228 (1932).

quite analogous to that of the aldehyde group in the above cases. The difference, emphasized by Kohler and Potter, between mesitylenic and phenyl ketones shows that the electromeric effect of the keto group in the former is much stronger and near to that of the aldehyde group. The writer has no explanation to offer for this new and remarkable fact, but he wishes to point out that he has not attempted theoretically to explain the relative strengths of the electromeric effects even of the simple groups investigated by him, which were only classified according to experimental evidence.

DEPARTMENT OF GENERAL CHEMISTRY
UNIVERSITY OF ISTANBUL
ISTANBUL, TURKEY
RECEIVED JANUARY 21, 1937

A Crystalline Compound of Semicarbazide and Semicarbazide Hydrochloride

BY H. L. HALLER AND F. B. LAFORGE

In preparing semicarbazones of the pyrethrins and related compounds in this Laboratory it was found[1] that the substitution of pyridine for sodium acetate increased the rate of reaction and resulted in much better yields of the semicarbazones. While using this procedure it was observed that sometimes crystals were deposited immediately from the solution. However, this did not occur in all cases. That this is not due to the formation of a semicarbazone is evidenced by the fact that the same material was sometimes obtained when a concentrated aqueous solution of semicarbazide hydrochloride was added to a mixture of pyridine and ethanol in the absence of ketones. Whether or not the crystallization occurred was found to depend upon the amount of water in the system. The crystalline product was always obtained when 2.5 g. of semicarbazide hydrochloride in 2.5 cc. of hot water was added to 17 cc. of 95% ethanol and 3 cc. of pyridine. The compound appears in the form of large prisms which are almost insoluble in alcohol and in pyridine but are easily soluble in water and aqueous alcohol provided the amount of water exceeds about 10%. It contains ionic chlorine and may be titrated with standard alkali solution. It melts at 132°.

Anal. Calcd. for $C_2H_{11}N_6O_2Cl$: equiv. wt., 186.5; N, 45.05; Cl, 19.03. Found: (36.8 mg. required 2.01 cc. of 0.1 N potassium hydroxide solution) equiv. wt., 183.1; N (Dumas), 45.06; Cl, 18.85.

This empirical formula is satisfied by the postulation that the compound contains one molecule of semicarbazide and one molecule of semicarbazide hydrochloride.

When the compound is dissolved in a small quantity of warm concentrated hydrochloric acid, the solution on cooling deposits semicarbazide hydrochloride, decomposing at 176°.

CONTRIBUTION FROM THE
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
RECEIVED FEBRUARY 11, 1937

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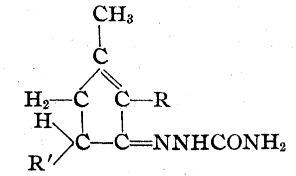
[1] H. L. Haller and F. B. LaForge, *J. Org. Chem.*, **1**, 38 (1936).

The Solubility of Certain Semicarbazones in Dilute Hydrochloric Acid

BY F. B. LAFORGE AND H. L. HALLER

In our investigations of the constituents of pyrethrum flowers, the semicarbazones of the pyrethrins and related compounds have served for their isolation and identification. Although pyridine has been substituted in all cases for the more commonly used sodium acetate in preparing these semicarbazones,[1] the employment of this base has had no effect on the properties of the derivatives obtained. Semicarbazones have been classed as neutral compounds, and those that are not soluble in water are supposed to be insoluble in dilute acids and alkalies.

In working with the semicarbazone of tetrahydropyrethrone (dihydrojasmone), formula I, $R = C_5H_{11}$, $R' = H$, we first observed that it was easily dissolved in cold dilute hydrochloric acid (about 4 N).



I

In the acid solution the semicarbazone is, of course, hydrolyzed on long standing and rapidly at elevated temperatures. It is, however, precipitated unchanged and in quantitative yield from the cold solution by prompt addition of alkali.

We were led by this observation to examine other related semicarbazones and have found

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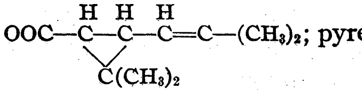
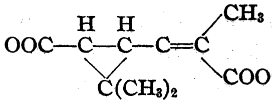
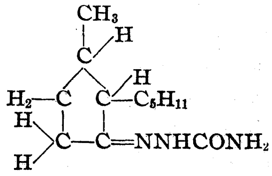
[1] H. L. Haller and F. B. LaForge, *J. Org. Chem.*, **1**, 38 (1936).

them to differ sharply with respect to their solubility in acids. The semicarbazones which we have considered may be divided into two groups, those that are soluble and those that are insoluble in dilute hydrochloric acid.

The former include the semicarbazones of pyrethrone, formula I, R = C_5H_7, R' = H; dihydropyrethrone (jasmone), R = C_5H_9, R' = H; tetrahydropyrethrone (dihydrojasmone), R = C_5H_{11}, R' = H; and tetrahydropyrethrolone, R = C_5H_{11}, R' = OH. The acid-insoluble semicarbazones include those of pyrethrolone, formula I, R = C_5H_7, R' = OH; pyrethrin I, R = C_5H_7, R' = ; pyrethrin II, R = C_5H_7, R' =  and two geometric forms of hexahydropyrethrone semicarbazone of melting points 160 and 194°, respectively, represented by formula II.



II

There seems to be no chemical feature distinguishing the members of each group. The solubility of some of the semicarbazones has been utilized in their separation from other material. All of an acid-soluble semicarbazone present in an impure reaction mixture may be obtained practically pure by extraction with dilute hydrochloric acid, removal of the by-products with a water-immiscible solvent, and precipitation of the semicarbazone with alkali. For example, a reaction product consisting of tetrahydro- and hexahydropyrethrone semicarbazones was separated into the two components by dissolving the one in dilute acid and filtering from the other.

To what extent the property of solubility in hydrochloric acid is shared by the semicarbazones of other ketones is a matter of interest, but one which we have not investigated.

CONTRIBUTION FROM THE
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
RECEIVED FEBRUARY 11, 1937

Photoreaction of Chlorine Monoxide and Hydrogen

BY T. IREDALE AND T. G. EDWARDS

According to Finkelnburg, Schumacher and Stieger[1] chlorine monoxide dissociates, in the continuous absorption region of the visible spectrum, into Cl and ClO. We have found that addition of hydrogen accelerates the decomposition, at any rate, up to the stage where the secondary reaction $H_2 + Cl_2 = 2HCl$ becomes prominent. As without the H_2, Cl_2 and O_2 are the main products, but there are now also small amounts of HCl and H_2O. Finally all the Cl_2 goes to HCl.

Since the reaction $Cl + H_2 = HCl + H$ has a collision efficiency of $10^{-4} - 10^{-5}$, and $Cl + Cl_2O = Cl_2 + ClO$[1] a collision efficiency of $10^{-2} - 10^{-3}$, H atoms are not so important as the ClO radical in continuing the chain, that is, where the Cl_2O and H_2 pressures are comparable. The chain must, therefore, be continued by the reactivity of ClO and H_2, a state of affairs not much understood in the literature of this subject.

We may have either $ClO + H_2 = HClO + H$ or $ClO + H_2 = HCl + OH$. The latter reaction seems the more probable. Further details will be forthcoming when we have studied the reaction more closely.

Contrary to the experience of others,[2] we did not find that Cl_2O was explosively unstable in the presence of strong light. A 500 candle power lamp brought within 2.5 cm. of a spherical glass bulb (7.6 cm. in diameter) containing Cl_2O at a pressure of half an atmosphere, did not cause an explosion, nor did it do so when hydrogen was present at the same pressure.

(1) Finkelnburg, Schumacher and Stieger, *Z. physik. Chem.*, **B15**, 127 (1931).

(2) Wallace and Goodeve, *Trans. Faraday Soc.*, **27**, 653 (1931).

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF SYDNEY
SYDNEY, AUSTRALIA
RECEIVED SEPTEMBER 9, 1936

The Heat of Mixing of Diisobutylene and Isooctane

BY WM. D. KENNEDY AND GEORGE S. PARKS

In connection with the recent study by Crawford and Parks[1] of the liquid-phase hydrogenation of diisobutylene (*i. e.*, a material containing about 4 parts of 2,4,4-trimethylpentene-1 and 1 part

(1) B. L. Crawford and G. S. Parks, THIS JOURNAL, **58**, 373 (1936).

of 2,4,4-trimethylpentene-2) to yield isoöctane (2,4,4-trimethylpentane), the assumption was made that mixtures of this paraffin with the parent olefins formed practically "perfect" solutions. Accordingly such solutions should be formed from the components without any appreciable heat of mixing and the partial vapor pressures of the components should follow Raoult's law. In view of the structural similarity of the paraffins and the olefins here involved, this assumption of perfect solutions certainly appeared reasonable on *a priori* grounds. Moreover, Beatty and Calingaert[2] had shown that the total pressures of mixtures of *n*-heptane and *n*-heptene-3 near the boiling point do not exhibit at any concentration more than a 0.5% positive deviation from the requirements of Raoult's law. However, the departure from ideality of such solutions may be appreciably greater at lower temperatures. In view of this possibility and the simplicity of the measurements, we decided to make also some direct calorimetric determinations of the heats of mixing of diisobutylene and isoöctane.

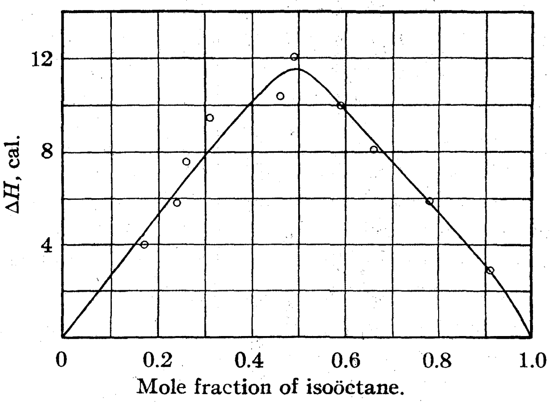


Fig. 1.—The heat absorption per mole of solution formed plotted against the mole fraction of isoöctane.

The vacuum jar calorimeter and the method of mixing employed previously by Parks and Chaffee[3] were used again in the present study. The mixing took place at 23° and the temperature change on formation of the solutions was measured to 0.001° by a copper–constantan thermocouple in conjunction with a White potentiometer. The necessary specific heat data for isoöctane and diisobutylene were taken from previous studies[4] in this Laboratory. Our hydrocarbon samples were carefully prepared materials which had been presented to us by the Shell Development Company. They had boiling ranges of about a degree and crystallized completely when cooled with liquid air; the respective densities at 20° were 0.6912 for the isoöctane and 0.7168 for diisobutylene.

Ten separate determinations of the heat of mixing were made in forming solutions ranging from 0.17 to 0.91 mole fraction of isoöctane. In the isothermal mixing process there appeared, for all concentrations, a small endothermic effect, which we have represented graphically in the accompanying figure. In our experiments this heat absorption reached a maximum for the formation of a solution containing 0.49 mole fraction of the isoöctane. In this case we found $\Delta H_{296} = 12.1\ (\pm 1.0)$ cal. for the process

$$0.49\ C_8H_{18}(l) + 0.51\ C_8H_{16}(l) = 1 \text{ mole of solution}$$

The minuteness of such a heat effect can be further emphasized by noting that it is only 1.3% of the effect previously recorded in the formation of a comparable solution of benzene and *n*-hexane.[5]

The previous assumption that such diisobutylene–isoöctane solutions are practically perfect is thus well justified.

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[2] H. A. Beatty and G. Calingaert, *Ind. Eng. Chem.*, **26**, 505 (1934).

[3] G. S. Parks and C. S. Chaffee, *J. Phys. Chem.*, **31**, 439 (1927).

[4] G. S. Parks, H. M. Huffman and S. B. Thomas, THIS JOURNAL, **52**, 1032 (1930); G. S. Parks and H. M. Huffman, *ibid.*, **52**, 4381 (1930).

[5] "International Critical Tables," Vol. V, page 157.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIV., CALIF.
RECEIVED FEBRUARY 8, 1937

The Transport Number of Silver in Solutions of Sodium Thiosulfate Practically Saturated with Silver Chloride

BY PIERRE VAN RYSSELBERGHE AND S. M. KNAPP

Evidence obtained by Müller and by Carrière and Raulet[1,2] from electrometric titration and conductivity shows that in aqueous mixtures of sodium thiosulfate with a silver salt, the silver is present as a monovalent anion $AgS_2O_3^-$.

We have obtained direct evidence for the existence of such an ion by measuring the transport number of silver in solutions of sodium thiosulfate saturated with silver chloride at 23°. The experiments were run at 25° according to a technique similar to that of Van Rysselberghe

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[1] Müller, *Z. anorg. Chem.*, **133**, 202 (1924).

[2] Carrière and Raulet, *Compt. rend.*, [7] **192**, 423 (1931).

and Nutting.[3] Salts of the highest purity were used and standard methods of analysis were followed in the determination of the changes in silver content of cathode, anode and middle portions. The results obtained in four experiments are reported in Table I.

TABLE I

DATA FOR THE MIGRATION OF SILVER IN SOLUTIONS OF SODIUM THIOSULFATE PRACTICALLY SATURATED WITH SILVER CHLORIDE AT 25°

No. of experiment	1	2	3	4
Weight Ag in coulometer, g.	0.0739	0.0523	0.0514	0.0504
Moles $Na_2S_2O_3$ per liter	.0976	.1000	.1034	.0967
Equivalents Ag per liter	.0795	.0808	.0843	.0787
Loss Ag at cathode, g.	.0150	.0111	.0126	.0093
Gain Ag at anode, g.	.0165	.0109	.0101	.0123
Average transport number of Ag^+	−.213	−.210	−.221	−.215
Ratio equivalents of $AgS_2O_3^-$ to total number equivalents	.204	.202	.204	.204

The changes in the anode and cathode portions were of the order of 2 to 3% of the original silver content. The changes in the middle portion were equal to zero within the limits of accuracy of the analysis. The numbers in the last line of the table were obtained on the assumption that the whole amount of silver is combined as $AgS_2O_3^-$; the total number of equivalents refers to all ionic species actually present (for instance, in experiment No. 2 we have 0.2 Na^+ + 0.0808 $AgS_2O_3^-$ + 0.0384 $S_2O_3^=$ + 0.0808 Cl^-).

Averaging the results of the four experiments we may say that a 0.1 molar solution of sodium thiosulfate saturated with silver chloride at 23° contains 0.08 equivalent of silver per liter and that the transport number of Ag^+ in such a solution is −0.215 at 25°.

(3) Van Rysselberghe and Nutting, THIS JOURNAL, **55**, 996 (1933).

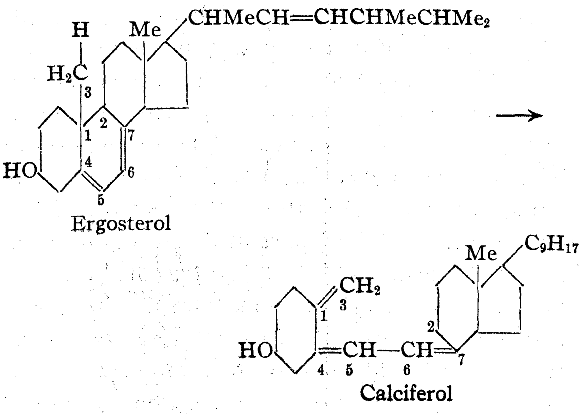
DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
CALIFORNIA

RECEIVED JANUARY 19, 1937

Calculation of the Activation Energy of the Rearrangement of Ergosterol to Calciferol

BY J. R. OWEN AND ALBERT SHERMAN

According to the work of Windaus and Grundmann[1] and of Heilbron, Jones, Samant and Spring[2] the rearrangement of ergosterol to calciferol may be represented by the equation



Ergosterol

Calciferol

This change involves the breaking of the 1,2-carbon–carbon bond and a shift of a hydrogen atom from carbon atom 3 to carbon atom 2, with the subsequent formation of a double bond between carbon atoms 1 and 3.

We have constructed molecular models and calculated the activation energy for the probable mechanism of such a transformation according to the semi-empirical method of Eyring.[3] The constants for the Morse curves used in the calculations are given in Table I.

TABLE I

Bond	r_0, Å.	ω_0 cm.$^{-1}$	D, kcal.
C–C	1.54[a]	990[b]	83.0[c]
	1.46[d]	[e]	74.5[f]
	1.44[g]	990[b]	74.5[f]
C–H	1.12[h]	2930[c]	92.3[h]

[a] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932). [b] Mecke, *Z. physik. Chem.*, **17B**, 1 (1932). [c] Pauling, THIS JOURNAL, **54**, 3570 (1932). [d] This value is the average of the C–C distances in a single and a double bond, and was used as the final 1,3-carbon–carbon distance. [e] This value was not needed since no Morse curve was drawn for this bond. [f] This value is one-half the strength of the carbon–carbon double bond and was used in all activation energy calculations involving the final 1,3-carbon–carbon bond, as well as in the construction of the Morse curve for the C–C bond in the ring broken. [g] This value is the carbon–carbon distance in benzene and was used in the construction of the Morse curve for the C–C bond in the ring broken. [h] Mulliken, *Rev. Modern Phys.*, **4**, 1 (1932).

According to Steenbock and co-workers[4] the long wave length limit for the conversion of ergosterol into calciferol by ultraviolet irradiation is 3100 Å. This corresponds to an energy of

(1) Windaus and Grundmann, *Ann.*, **524**, 295–99 (1936).

(2) Heilbron, Jones, Samant and Spring, *J. Chem. Soc.*, 905–907 (1936).

(3) See, *e. g.*, the article by Van Vleck and Sherman, *Rev. Modern Phys.*, **7**, 167 (1935).

(4) Steenbock and co-workers, *J. Biol. Chem.*, **63**, 25 (1925).

approximately 92 kcal. and represents a maximum value of the activation energy, since some of the energy absorbed may be dissipated as heat.

We have considered many mechanisms for this rearrangement and the value which we calculate for the transformation involving the lowest activation energy is 72 kcal. The mechanism of this rearrangement will be described in some detail.

Initially the carbon atoms 1, 2 and 3 and the hydrogen atom taking part in the reaction are in the same plane. The C–H group rotates about the 1,3-carbon–carbon bond until the three carbon atoms are at the corners of an equilateral triangle with the hydrogen atom equidistant (approximately 1.12 Å.) from carbon atoms 2 and 3. Up to this point all four atoms remain in the same plane. The next three steps occur simultaneously: (1) the hydrogen atom moves away from carbon atom 3, at the same time maintaining a constant distance from carbon atom 2; (2) carbon atoms 1 and 2 separate to a distance of approximately 2.07 Å.; and (3) the two parts of the molecule formed by the breaking of the 1,2-carbon–carbon bond rotate about the 5,6-carbon–carbon bond so that the plane of carbon atoms 2, 6 and 7 is at an angle of approximately 26° with that of the carbon atoms 1, 4 and 5. Following these steps the hydrogen atom moves to a final position determined by the ring of which carbon atom 2 is a part, and by the valence angles of this carbon atom. The system is now in the activated state and from this point onward (that is, as the rotation about the 5,6-carbon–carbon bond continues) the energy of the system decreases.

There are two factors which we have not considered that will affect the energy required for activation. The double bond which is formed between carbon atoms 1 and 3 is part of a conjugated system (atoms 3,1,4,5,6,7) and, although quantitative calculations have not been made, we know that this will tend to lower the activation energy slightly. The large size of the molecule introduces steric factors which probably will cause an increase in the activation energy. These two factors will tend to cancel each other, and we have not attempted to estimate them quantitatively. Their effect will not be large.

From the nature of the rearrangement it is evident that another mechanism could involve the breaking of a C–H bond (92.3 kcal.) and a reaction of the H atom with carbon atom number 2. This mechanism would therefore involve an energy of 92.3 kcal., and hence we conclude that the activation energy for the conversion of ergosterol to calciferol lies between 72 and 92 kcal. This is consistent with the value found by Steenbock for the long wave length limit.

One of us (A. S.) wishes to acknowledge support from the Wisconsin Alumni Research Foundation and the other gratefully acknowledges support from the Phi Kappa Phi honor society.

PHYSICAL CHEMICAL LABORATORY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
RECEIVED JANUARY 13, 1937

A Simple Method for the Preparation of the Chloro Ketone $C_{19}H_{27}OCl$, Dehydroandrosteryl Chloride

BY EVERETT S. WALLIS AND E. FERNHOLZ

In a recent paper by A. Butenandt and W. Grosse[1] the statement is made that replacement of the hydroxyl group in dehydroandrosterone by chlorine by the usual methods is unsatisfactory, low yields of the chloro ketone being obtained. From what is written one gets the impression that the difficulties involved are, indeed, serious, for the authors considered other possibilities and developed a new method which involves the following steps

Dehydroandrosterone ⟶ toluenesulfonate (71%) ⟶ *epi*-dehydroandrosterone methyl ether[2] (99%) ⟶ dehydroandrosteryl chloride (79%); yield over all (56%)

As is readily seen the yield of the chloride is not too satisfactory and even if we could consider the yield as fair the method would still be involved.

In the course of some of our experiments we have had occasion also to prepare this important chloro ketone. In our hands the treatment of dehydroandrosterone with phosphorus pentachloride has always given very satisfactory results. When the reaction is carried out in chloroform solution the yield is 83%, and the preparation involves but one step.

Experimental Part

One gram of dehydroandrosterone was added to a mixture of 10 cc. of dry chloroform and 1 g. of phosphorus

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[1] A. Butenandt and W. Grosse, *Ber.*, **69**, 2776 (1936).

[2] The experimental results of Wallis, Fernholz and Gephart [THIS JOURNAL, **59**, 137 (1937)] obtained in a study of the action of potassium acetate on cholesteryl *p*-toluene-sulfonate show that a molecular rearrangement takes place during this reaction. In the light of these experiments the naming of this methyl ether may not be justified. It is entirely possible that the compound may have a different structure.

pentachloride. A violent reaction took place. The resulting mixture was kept at room temperature for one hour. Water was then added (100 cc.), the two layers were separated, and the chloroform layer removed to the steam-bath. During the evaporation of the chloroform the chloride crystallized. It was filtered and dissolved in ether. The ether solution was washed with sodium hydroxide to remove acidic esters. The ether residue after one crystallization gave an almost pure chloride; yield 0.76 g.; m. p. 153°. The mother liquor was evaporated and the residue was distilled in high vacuum and recrystallized from methyl alcohol; yield 0.12 g.; total yield 0.88 g. (83%). Further repeated recrystallizations did not raise the melting point above 154° (uncorr.); $[\alpha]^{22}\text{D}$ $+14.6°$ (19.2 mg. in 2 cc. of chloroform solution gave $\alpha^{22}\text{D}$ $+0.14°$, 1-dm. tube).

Summary.—A simple method is described for the preparation of dehydroandrosteryl chloride in good yield. The chloro ketone so prepared melts at 154° and has a specific rotation $[\alpha]^{22}\text{D}$ $+14.6°$.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
RECEIVED JANUARY 28, 1937

The Separation of the C_{17}-Epimers of Oestradiol by Digitonin

BY O. WINTERSTEINER

It has been shown by Schwenk and Hildebrandt[1] that two epimeric forms of oestradiol can be obtained by catalytic reduction of the 17-keto group of oestrone (theelin). The lower melting α-isomer (m. p. 178°, $[\alpha]\text{D}$ $+81°$), which occurs in follicular fluid[2] and in the urine of pregnant mares,[3] is the most potent oestrogenic compound known. The higher melting β-isomer (m. p. 223°, $[\alpha]\text{D}$ $+54°$), which is much less active physiologically, has only recently been prepared in pure form. Its properties will be described in more detail in a separate communication.[4] We have found recently that the two isomers can be separated conveniently by digitonin, whereby the laborious separation by fractional crystallization may be avoided. Only the lower-melting α-isomer forms a sparingly soluble digitonide, when treated with a solution of digitonin in 80% alcohol. The molecular compound deposits slowly in form of beautiful needles, which melt at about 265° after partial decomposition at 195°, and from which the diol can be regenerated easily by the usual methods. Also the 3-benzoate of the α-isomer yields a crystalline precipitate with digitonin, though more slowly than the free diol. Neither the high melting β-oestradiol nor its 3-benzoate precipitates with digitonin under identical conditions. These results show clearly that it is the configuration of the 17-carbon atom which determines the capacity to form insoluble digitonides of this type.

The digitonin reaction is also negative with oestriol (theelol), dihydroequilenin (δ-follicular hormone)[5] and 17-*trans*-testosterone.[6] Furthermore, no precipitate was obtained with a crude preparation of androstenediol-3-acetate, which according to the mode of its preparation should have contained some of the 17-*cis*-epimer. The melting point of dihydroequilenin, and that of its benzoate, its low specific rotation ($[\alpha]\text{D}$ $-4.7°$), its low physiological potency, and its failure to precipitate with digitonin would place this compound in the β-series of oestrogenic diols. On the other hand, if the same criteria be applied to 17-*trans*-testosterone, all the data except the negative digitonin reaction speak for its steric relationship to α-oestradiol. Caution is obviously necessary in interpreting the behavior of C_{17}-epimers toward digitonin as an indication of stereochemical relationships.

In the pregnane series, Butenandt and coworkers[7] have employed digitonin for the separation of C_{17}-epimers. *allo*-Pregnanedione, *allo*-pregnanol-3-one-20-3-acetate, and Δ^5-pregnenol-3-one-20, but not their C_{17}-epimers, termed *iso*-compounds by these workers, form insoluble digitonides.

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(1) Schwenk and Hildebrandt, *Naturwiss.*, **21,** 177 (1933).

(2) MacCorquodale, Thayer and Doisy, *Proc. Soc. Exptl. Biol. Med.*, **32,** 1182 (1935); *J. Biol. Chem.*, **115,** 435 (1936).

(3) Wintersteiner, Schwenk and Whitman, *Proc. Soc. Exptl. Biol. Med.*, **32,** 1087 (1935).

(4) Whitman, Wintersteiner and Schwenk, forthcoming publication.

(5) Wintersteiner, Schwenk, Hirschmann and Whitman, THIS JOURNAL, **58,** 2652 (1936).

(6) Ruzicka and Kägi, *Helv. Chim. Acta*, **19,** 842 (1936).

(7) Butenandt and Mamoli, *Ber.*, **68,** 1847 (1935); Butenandt and Fleischer, *ibid.*, **70,** 96 (1937).

DEPARTMENT OF BIOLOGICAL CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.
RECEIVED JANUARY 28, 1937

Reaction of Lanthanum Oxide with Ammonium Iodide

BY RALPH C. YOUNG AND JANE L. HASTINGS

By following the general method of Reed, Hopkins and Audrieth[1] for the preparation of the chlo-

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(1) Reed with Hopkins and Audrieth, THIS JOURNAL, **57,** 1159 (1935).

rides and the bromides of the rare earth metals it has been found possible to carry out the reaction between lanthanum oxide and ammonium iodide in such a manner that the final product contains about 90% of anhydrous lanthanum iodide.

The essential features of the procedure are as follows. One gram of ammonium iodide is poured into a Pyrex tube, 10 mm. in bore and 60 cm. long, closed at one end. There is then added a mixture of 1 g. of lanthanum oxide and 6 g. of ammonium iodide. The tube is inserted in an electric furnace to a distance of 22 cm., being slightly inclined downward at the outer open end, and is heated at 350°, with an occasional rotation, until no more water condenses in that part of the tube outside the furnace. Four hours are required for complete reaction, whereupon the excess ammonium iodide is removed by sublimation in a high vacuum at 250°. During the whole process the vapor from the ammonium iodide, passing over the product, protects it from reaction with oxygen which would otherwise occur even at low pressures. When no more ammonium iodide condenses outside the heated zone, the tube is sealed and quickly cooled to room temperature.

The product obtained by this method is nearly white with a very slight yellow tinge. Its hydration on exposure to air and the vigor of its reaction with water are indicative of the presence of anhydrous lanthanum iodide. On extraction with water 10% or less is insoluble. The atomic ratio of iodine to lanthanum in this insoluble residue varies from 0 to approximately 0.3. In the solution the ratio is 3, and, since no ammonium ion is present, it corresponds to the formula, LaI_3. Lanthanum iodide was also extracted from the raw product with 95% ethyl alcohol.

RESEARCH LABORATORY OF INORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
RECEIVED DECEMBER 17, 1936

COMMUNICATIONS TO THE EDITOR

INHIBITION OF THERMAL DECOMPOSITION OF *n*-BUTANE BY NITRIC OXIDE

Sir:

The recent work of Fletcher and Rollefson [THIS JOURNAL, **58**, 2129, 2135 (1936)] has shown that the acceleration of an organic vapor phase decomposition by ethylene oxide, and inhibition of the normal decomposition by nitric oxide give rather conclusive evidence that the decomposition proceeds via a chain mechanism.

We have previously shown [*ibid.*, **58**, 1317 (1936)] that ethylene oxide accelerates the decomposition of propane, *n*- and *i*-butane.

We now find that the decomposition of *n*-butane is strongly inhibited by small amounts of NO, as shown by the following table.

P_0 butane = 200 mm.; temp., 500 ± 1.0°; KCl-coated reaction bulb

P_0(NO), mm.	Init. rate, mm./min.	% Dec. at 120 min. By ΔP	By anal.
0	1.0	26.5	31
20	0.05	7.1	13

The rates as measured by the analysis after 120 minutes indicate that the inhibition is somewhat less than would be concluded from the initial rates. However, the fact that the normal reaction falls off quite rapidly with time, while the inhibited reaction rate increases continuously, can in large part explain this discrepancy. Thus the actual inhibition must lie between a 20/1 ratio of normal to inhibited rate and a 3/1 ratio, as given by the runs to high percentage decomposition. Measurements over a wide range of P_0(NO) indicate a region of maximum inhibition at about 20 mm.

This result, together with the arguments advanced by Hinshelwood [Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **A154**, 335 (1936)] as to the possible causes of an observed inhibition, lead us to the conclusion that the decomposition of butane under these conditions is largely a chain reaction.

Further work is now in progress, attempting to correlate the two effects in a more quantitative manner. It is also hoped to extend the work to lower hydrocarbons, particularly ethane.

FRICK CHEMICAL LABORATORY L. S. ECHOLS
PRINCETON, N. J. R. N. PEASE

RECEIVED MARCH 11, 1937

CHEMICAL STUDIES ON TOAD POISONS. FURTHER CONTRIBUTIONS TO THE CHEMICAL CONSTITUTION OF MARINOBUFAGIN, CINOBUFAGIN AND GAMABUFAGIN

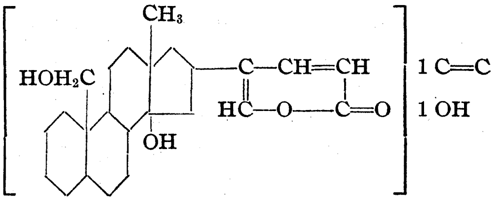
Sir:

Marinobufagin, $C_{24}H_{32}O_5$ [Jensen and Evans, Jr., *J. Biol. Chem.*, **104**, 307 (1934)], and cinobufagin, $C_{26}H_{34}O_6$ [Crowfoot and Jensen, THIS JOURNAL, **58**, 2018 (1936)], are unsaturated hydroxy lactones, cinobufagin being the acetyl derivative of the compound $C_{24}H_{32}O_5$, an isomer of marinobufagin. Tschesche and Offe [*Ber.*, **68**, 1998 (1935)] and independently Jensen [THIS JOURNAL, **57**, 2733 (1935)] showed that cinobufagin on dehydrogenation with selenium yields the Diels hydrocarbon $C_{18}H_{16}$. It has been found that marinobufagin (5 g. used) under the conditions described for cinobufagin [Jensen, *ibid.*, **57**, 2733 (1935)] also yields this hydrocarbon, found m. p. 122–123°, no depression when mixed with methylcyclopentenophenanthrene (m. p. 123–124°). *Anal.* Calcd. for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.92; H, 7.17.

Repetition of catalytic hydrogenation of marinobufagin and cinobufagin has revealed the presence of three double bonds instead of two as previously reported by Jensen and Evans [*J. Biol. Chem.*, **104**, 307 (1934)]; α-hexahydromarinobufagin m. p. 212–213°, β-derivative m. p. 225–227°; α-hexahydrocinobufagin m. p. 230–232°; β-derivative m. p. 210–212°. The found analytical data agree with the calculated. Simultaneously small amounts of acidic products are produced, probably by the opening of the lactone ring. Tschesche and Offe [*Ber.*, **69**, 2361 (1936)] have since reported similar findings.

Ozonization of marinobufagin and cinobufagin (ozone was passed under cooling for three hours through a solution of 1 g. of substance in chloroform, the working up of the reaction product was carried out in the usual manner) was found to yield formic acid, identified by qualitative tests, and glyoxylic acid, identified by color reactions and as the dinitrophenylhydrazone, yellow needles m. p. 190° with decomposition, no depression with the derivative prepared from glyoxylic acid. A small amount of oxalic acid, formed by oxidation of glyoxylic acid, was also found and identified as the calcium salt. These findings indicate the presence of two double bonds in the lactone group, which is a six-membered ring and apparently identical with that in scillaren [Stoll, Hofmann and Peyer, *Helv. Chim. Acta*, **18**, 1247 (1935)]. The third double bond is present in the sterol ring; its exact position is still uncertain.

It has been found that both marinobufagin and gamabufagin contain a —CH_2OH group attached either at C_{10} or at C_{13}, corresponding to one of the angular methyl groups of the sterols. Under the influence of strong acid or alkali this primary alcoholic group is eliminated as formaldehyde. On oxidation with chromic acid marinobufagin gives an aldehyde, the oxidation product giving the typical reactions for an aldehyde group. Evidence has been obtained that a tertiary hydroxyl group is attached at C_{14} in all three principles. Whether or not the third hydroxyl group in marinobufagin is also tertiary is somewhat uncertain, as is its position. Under the influence of acid two hydroxyl groups in marinobufagin are eliminated as water. On the basis of the experimental findings the following structure for marinobufagin is suggested



Analytical data obtained for gamabufagin, acetylgamabufagin and anhydrogamabufagin indicate the empirical constitution of $C_{24}H_{34}O_5$ for gamabufagin, as suggested by Wieland and Vocke [*Ann.*, **481**, 215 (1930)]. Gamabufagin contains only two double bonds, both in the lactone ring. Under the influence of acid gamabufagin loses one molecule of water. Both cinobufagin and gamabufagin have a structure similar to that of marinobufagin.

The author is greatly indebted to Dr. K. K. Chen, Lilly Research Laboratories, Indianapolis, for a supply of the secretion of the Japanese toad.

Owing to the temporary interruption of this investigation, it is necessary to defer publication of the details of the work until a later date.

LABORATORY FOR ENDOCRINE RESEARCH
SCHOOL OF MEDICINE
JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
H. JENSEN

RECEIVED MARCH 10, 1937

STEROLS. XII. SYNTHETIC PREPARATION OF *EPI*-ALLO-PREGNANOLONE, THE ANDROGENIC PRINCIPLE OF HUMAN PREGNANCY URINE

Sir:

That human pregnancy urine contains a substance which has male hormone activity has been reported by several workers. Because of the similarity in physiological activities in the male hormone tests between human pregnancy and male urine extracts, it has been assumed that the male principle in pregnancy urine was androsterone. Heretofore this androgenic principle has not been isolated.

Recently, Marker, Kamm and McGrew [THIS JOURNAL, **59,** 616 (1937)] reported the isolation and identification of *epi*-allo-pregnanolone from the sterol fraction of human pregnancy urine after the removal of theelin and theelol. At the time of this report we did not have the physiological assays on this compound. Since then it has been found that the substance isolated from human pregnancy urine promotes the growth of the seminal vesicle in the rat tests. Preliminary tests have shown this to have about the same activity as androsterone.

We have now prepared synthetically *epi*-allo-pregnanolone from 3-chloro-allo-cholanic acid, a by-product from the preparation of chloroandrosterone [Marker, Whitmore and Kamm, THIS JOURNAL **57,** 2358 (1935)]. This was prepared by the stepwise degradation of the side-chain according to the method of Wieland [*Z. physiol. Chem.*, **161,** 80 (1926)].

3-Chloro-allo-cholanic acid, m. p. 180°, was converted into its methyl ester, m. p. 133°. *Anal.* Calcd. for $C_{25}H_{41}O_2Cl$: C, 73.2; H, 10.1; Found: C, 72.8; H, 10.3. This was treated with a phenyl Grignard reagent and the resulting carbinol melted at 171°. *Anal.* Calcd. for $C_{36}H_{49}OCl$: C, 81.1; H, 9.2. Found: C, 81.1; H, 9.3. It was oxidized by chromic acid to 3-chloro-allo-*nor*-cholanic acid. *Anal.* Calcd. for $C_{23}H_{37}O_2Cl$: C, 72.5; H, 9.8. Found: C, 72.8; H, 9.6. This acid was converted to its methyl ester, m. p. 178°. *Anal.* Calcd. for $C_{24}H_{39}O_2Cl$: C, 73.0; H, 10.0. Found: C, 73.3; H, 10.2. By treating with a phenyl Grignard reagent, 3-chloro-allo-bis-*nor*-cholanyldiphenylcarbinol was obtained, m. p. 183°. *Anal.* Calcd. for $C_{35}H_{47}OCl$: C, 80.9; H, 9.1. Found: C, 80.8: H, 9.3. This carbinol was oxidized by chromic acid to 3-chloro-bis-*nor*-allo-cholanic acid, m. p. 231°. *Anal.* Calcd. for $C_{22}H_{35}O_2Cl$: C, 71.9; H, 9.6. Found: C, 71.8; H, 9.3. This acid was converted to its methyl ester, m. p. 150°. *Anal.* Calcd. for $C_{23}H_{37}O_2Cl$: C, 72.5; H, 9.8. Found: C, 72.5; H, 9.8. By treating with a phenyl Grignard reagent the carbinol was obtained, m. p. 146°. *Anal.* Calcd. for $C_{34}H_{45}OCl$: C, 80.8; H, 9.0. Found: C, 80.9; H, 9.2. This carbinol was dehydrated by refluxing with acetic acid and acetic anhydride. The resulting product was ozonized and the ozonolysis product treated with potassium acetate to convert the chloro derivative into an *epi*-OH compound [Marker, Whitmore and Kamm, THIS JOURNAL, **57,** 2358 (1935)]. The hydroxy ketone was purified by means of its half succinic ester and then as the semicarbazone. It gave *epi*-allo-pregnanolone, m. p. 170°. *Anal.* Calcd. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.7. Found: C, 78.9; H, 10.9. This was identical with the natural product which we isolated from human pregnancy urine.

THE SCHOOL OF
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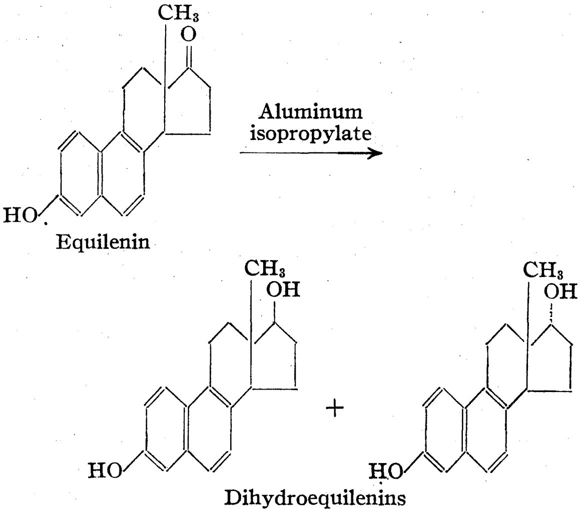
RECEIVED MARCH 18, 1937

STEROLS. XIII. THE DIHYDROEQUILENINS

Sir:

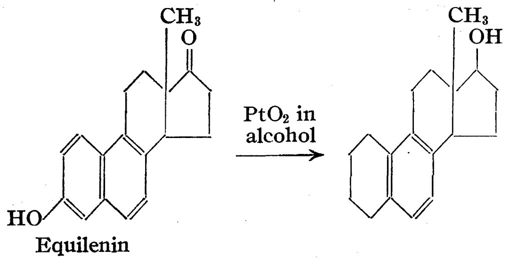
Recently Wintersteiner, Schwenk, Hirschmann and Whitman [THIS JOURNAL, **58,** 2652 (1936)] in their studies on the isolation of the δ-follicular hormone from the phenolic fraction of mare's urine obtained as the δ-follicular fraction a molecular compound of two components, one of which formed a picrate. This was isolated and identified as dihydroequilenin. They suggested that possibly the high estrogenic activity of the originally reported δ-follicular hormone [Wintersteiner, Schwenk and Whitman, *Proc. Soc. Exptl. Biol. Med.*, **32,** 1087 (1935)] is due to the other isomer of dihydroequilenin, differing from their product only in the configuration of the —OH group in the 17-position.

We have now prepared both isomers of dihydroequilenin by the reduction of equilenin with aluminum isopropylate. These isomers were separated by crystallization from alcohol, the more soluble dihydroequilenin melting at 215°. *Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.5; H, 7.5. Found: C, 80.4; H, 7.7. This gave a monobenzoate of m. p. 204°. *Anal.* Calcd. for $C_{25}H_{24}O_3$: C, 80.4; H, 6.7. Found: C, 80.4; H, 6.7. These products are identical in melting points with the products isolated by Wintersteiner and co-workers from mare's urine.



From the less soluble reduction product we obtained the epimers of Wintersteiner's dihydroequilenin. This product melts at 248°. *Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.5; H, 7.5. Found: C, 80.3; H, 7.6. This gives a diacetate of m. p. 124° [*Anal.* Calcd. for $C_{22}H_{24}O_4$: C, 74.9; H, 6.9. Found: C, 74.8; H, 7.0] and a monobenzoate m. p. 215° [*Anal.* Calcd. for $C_{25}H_{24}O_3$: C, 80.4; H, 6.7. Found: C, 80.5; H, 6.7]. This is the product that Wintersteiner suggests may be the other component of the δ-follicular hormone mixture which causes the high estrogenic activity. Each isomer gives a large melting point depression when mixed with the other, or with the original equilenin.

We attempted to prepare dihydroequilenin by the reduction of equilenin with sodium as tried by David [*Acta brevia Neerland.*, **4,** 63 (1934)]. We duplicated his results, obtaining only an oil. The sodium apparently effects a partial reduction of the naphthol ring. Catalytic hydrogenation of equilenin with Adams platinum oxide catalyst in alcohol reduced the first ring with the loss of an —OH group to give a 70% yield of a product containing only one oxygen atom.



The product melted at 148°. *Anal.* Calcd. for $C_{18}H_{24}O$: C, 84.3; H, 9.4. Found: C, 84.3; H, 9.6. Acetate, m. p. 104°. *Anal.* Calcd. for $C_{20}H_{26}O_2$: C, 80.4; H, 8.8. Found: C, 80.0; H, 9.0.

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OLIVER KAMM
THOMAS S. OAKWOOD
FRANK H. TENDICK

RECEIVED MARCH 23, 1937

NEW BOOKS

British Chemicals and Their Manufacturers. The Official Directory of the Association of British Chemical Manufacturers. Published by and available only from the Association, 166 Piccadilly, London W 1, England, 1937. 466 pp. *Gratis* to genuine purchasers of chemicals.

This book, the Official Directory of the Association of British Chemical Manufacturers, gives information as to the products manufactured by the members. It contains a list of the products, with the grades and the manufacturer of each product.

It also contains lists of Proprietary Trade Names and Trade-marks and complete indices.

All different sections are printed in English, French, Spanish, Italian, Portuguese and German.

Genuine purchasers of chemicals can obtain this book *gratis* from the office of the Association. For educational institutions, as well as industry, this book will be found a handy reference to the many chemicals manufactured by the association.

CLIFTON P. ADAMS

Organic Chemistry. The Chemistry of the Compounds of Carbon. By LUCIUS JUNIUS DESHA, Professor of Chemistry, Washington and Lee University. McGraw-Hill Book Company, 330 West 42d Street, New York, N. Y., 1936. xv + 750 pp. Illustrated. 14.5 × 22 cm. Price, $3.75.

"This textbook has been written for college students and primarily for those whose formal instruction in organic chemistry ends with a one-year course .... The guiding policy has been to consider compounds if, where, and as they serve usefully to illustrate and explain the general principles of organic chemistry." The book is conspicuously different from other present-day texts not in this, but in following W. A. Noyes's practice of treating aliphatic and aromatic compounds side by side. The first 128 pages are devoted to hydrocarbons, under the chapter headings: Saturation and Unsaturation—Isomerism—Homology—Natural Gas and Petroleum—Ring Formation; Alicyclic Hydrocarbons—The Aromatic Nucleus; Benzene and its Homologues—Polynuclear Hydrocarbons; By-products of Coking. In the following nine chapters, simple derivatives of the hydrocarbons, aliphatic and aromatic together, are considered in order. Eight chapters follow on polysubstituted and mixed compounds, and five chapters on "Special Results of Certain Structures." The chapter headings in this section are: Variable Strength of Linkages—Tautomerism—Rearrangements—Color and Constitution; Dyes and Dyeing—Stereoisomerism. The final four chapters deal with some important plant and animal products (carbohydrates, fats, lipides, proteins, terpenes, etc.). An appendix includes generalizations on the identification of organic compounds.

There is a restrained but consistent emphasis upon theory throughout the book, which leads to the inclusion of such topics as the theory of affinity–capacity and the mechanisms of molecular rearrangements, frequently reserved for later courses in organic chemistry. This willingness to tackle fundamental problems will be appreciated by the better students, but these are the very students whose instruction in organic chemistry ought *not* to end with a one-year course. In contrast to these inclusions, the experimental facts about conjugated systems are touched only very lightly, and the diene synthesis of Diels and Alder is not mentioned. The benzene problem is discussed at a point where simple conjugated systems are not available for comparison, although cycloöctatetraene is mentioned in a note. Many experimental tests are described throughout the book, but nothing is said about how the molecular formula of a compound is established.

The book is not entirely free from inaccuracies. In alkylating acetoacetic ester it is not usual, as stated on page 517, to add sodium wire to the anhydrous ester. By established usage, the Wurtz reaction (page 24) becomes the Wurtz–Fittig reaction only when carried out between an aliphatic and an aromatic halide. The "chair" form of the cyclohexane ring (page 79), according to models, does not shift into the other form without some slight bond distortion. In the main, however, the statements in the book are well considered. The illustrations are good and the style clear.

One of the greatest aids to a student in studying this necessarily descriptive subject is the consideration, more or less together, of a group of genetically related compounds. The shuttling back and forth between aliphatic and aromatic compounds throughout the book limits the possibility of this. Thus it seems to the reviewer that the distinguishing feature of this text, its order of presentation, is its one serious drawback.

P. D. BARTLETT

Thermodynamic Theory of Affinity. A Book of Principles. By TH. DE DONDER, Professor of Mathematical Physics, University of Brussels, and PIERRE VAN RYSSELBERGHE, Assistant Professor of Chemistry at Stanford University. Stanford University Press, Stanford University, California, 1936. xx + 142 pp. 4 figs. 16 × 24.5 cm. Price, $3.00.

This book presents in a readable form a fairly complete résumé of the theory of affinity developed by De Donder. The use of the international set of thermodynamic symbols makes the reading much easier in this than in the French editions for those not familiar with De Donder's earlier notation. The method of presentation is didactical. The first three chapters are devoted to the two laws of thermodynamics; the next five, to the properties of the affinity and the last eight, to the applications of the affinity function to a discussion of equilibrium, the phase rule, ideal and non-ideal gases, Le Chatelier's principle, heterogeneous and homogeneous equilibria and galvanic cells.

The representation of the status of a chemical reaction in a closed system by the "degree of advancement of the reaction" introduces a very desirable symmetry into such discussions.

The thermodynamic treatment is involved because of the introduction of the uncompensated heat of Clausius. This leads to relations as on pages 16 to 18 which have many unfamiliar added terms all of which are shown to be zero. On page 18 it is implied that the relations containing these zero terms are more general than those heretofore used. The method of Gibbs in which changes in state properties are treated by reversible processes whether or not the actual change under consideration is reversible is more direct and satisfying. An appreciable part of the book is devoted to warning the reader against a mistake which only the most naïve beginner would make, as on pages 34 to 36 where a straw man is thoroughly demolished. On page 54 some new equations of interest are given; a statement in words of the significance of these relations would be a valuable help to the reader.

Throughout the book the affinity function is used and the properties and uses of this function are developed at length. For a chemical change in state in a closed system the affinity A is given by the relation $A = -\Sigma \nu_i \mu_i$ (ν_i = stoichiometric coefficient and μ_i = chemical potential of the i-th constituent). The treatment throughout is almost entirely mathematical; the physical interpretation of some of the results, especially the connection between the affinity and the yield of a chemical reaction under different conditions, would add to the interest in this function.

J. A. BEATTIE

The Mechanism of Contact Catalysis. By R. H. GRIFFITH, D.Phil., Senior Research Chemist, The Gas Light and Coke Co. Oxford University Press, 114 Fifth Avenue, New York, N. Y., 1936. xi + 208 pp. 90 figs. 14 × 22.5 cm. Price, $5.00.

The avowed purpose of this book is to summarize developments in the theory of catalytic mechanism in the decade since the publication of such works as Rideal and Taylor's "Catalysis in Theory and Practice." Studies reported as late as 1936 are included, as well as a number of interesting, unpublished investigations by the author. Chapter heads are: experimental methods, adsorption, promoters and carriers, poisoning and retardation, examination of the catalyst surface, geometry of the catalyst surface, mechanism of catalysis, development of catalysts. The focus of attention is the catalyst and its behavior with reactants and products, rather than the reactions themselves. The author treads the middle road between the extremes of theory and practice, emphasizing laboratory researches to the exclusion of quantum mechanics on the one hand and data from technical operations on the other. His critical comments on recent work should be of interest, particularly to specialists in the field even though their own views may sometimes differ. The treatment is selective rather than exhaustive, but at least a majority of the principal contributions receive attention.

In the exposition of a subject as various and elusive as catalytic mechanism, a certain looseness of organization of material is probably unavoidable. The resulting diffuseness and repetition the author strives to minimize by frequent cross references, an author index and an elaborate subject index. But not all the traditional "mystery" of catalysis is removed. Apparently it must largely remain until more precise concepts are developed and generally understood, so that more precise statements can be used. For example (p. 36): "The significance of these facts [rates of diffusion of hydrogen and deuterium through copper] in connexion with catalytic changes occurring at a surface is probably much greater with regard to determining the character of the surface itself than with respect to any influence on the catalyzed reaction, once the surface has been formed."

The physical make-up of the book is irreproachable.

ARTHUR F. BENTON

Prelude to Chemistry. An Outline of Alchemy, its Literature and Relationships. By JOHN READ, Ph.D., M.A., Sc.D., F.R.S., Professor of Chemistry in the United College of St. Salvator and St. Leonard in the University of St. Andrews, Scotland. The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1937. xxiv + 327 pp. Illustrated. 16 × 24 cm. Price, $5.00.

Professor Read's book is devoted primarily to an account of the affiliations of early chemistry, and, for that reason perhaps, succeeds in supplying a correct understanding of the theories of early chemistry and alchemy, of their probable origins and of their nature and development. It does this better than any other single book with which we are acquainted. It contains very little of the actual chemical knowledge of the ancients, but by its thorough examination of the speculative background of that knowledge it throws a clearer light than would otherwise be possible upon the central and dominant doctrine. It shows how the doctrine operated in the laboratory, but also how it operated in the minds of the laboratory workers in their imaginative and metaphorical language, their curious diagrams and symbolic pictures. Professor Read follows the elaborations of alchemical doctrine in considerable detail in a number of special cases, the hieroglyphic pictures of Nicholas Flamel, the *Splendor Solis*, the "Hermetic Museum," the works of Thomas Norton, John Cremer and Basil Valentine, the alchemical pictures of Stolcius, Mylius and Michael Maier (whose interconnections he straightens out), and the alchemical music of the last-named in *Atalanta Fugiens*. The reader cannot fail to see that the alchemists, for all their intellectual and artistic excesses, were men of much sense: he will understand the ideas which were guiding them.

The book is scholarly, interesting and attractive. It is written in a fine literary style, pervaded by the author's gentle sense of humor and sympathetic insight. An Appendix contains an essay on "The Music in *Atalanta Fugiens*" by F. H. Sawyer, together with several of the fugues arranged in the modern manner for choral singing—also a Glossary and Bibliography and Notes. The work is profusely illustrated with a colored frontispiece, 63 other plates, 17 figures and additional small pictures.

"The Garden has been arrayed to lure *Bees* and *Butterflies* alike; but it may be added that a flowery Border, metamorphosed after the manner of alchemy into a bibliography, garnishes the out-going Arbour. Moreover, divers faire Rose-trees, transmuted into cross-references, have been planted in the middest of the Garden. The *Butterflies*, an they list, may hover over these blossoms without settling thereon; but peradventure the *Bees* will find them as full of Honey as of Fragrance."

TENNEY L. DAVIS

Introduction to Theoretical Chemistry. By WILLIAM BUELL MELDRUM, Professor of Chemistry, Haverford College, and FRANK THOMSON GUCKER, JR., Associate Professor of Chemistry, Northwestern University. American Book Company, 88 Lexington Ave., New York, N. Y. 1936. xiv + 614 pp. 155 figs. 15 × 22.5 cm. Price, $3.50.

This text is well worthy of its name. It carries the student through each of the main subdivisions of modern chemistry from the earliest developments to the most recent, without, however, becoming too specialized for the average undergraduate. It has, of course, the disadvantages of the historical presentation—the student must follow each mistake and false premise of the early workers before arriving at the currently accepted point of view on each subject. For this reason it will probably be found unsuited to the needs of beginning students, who are usually confused by a multiplicity of theories. On the other hand, this very treatment could make this book extremely valuable in teaching students who have already completed the elementary course in chemistry. They would be led to examine the theoretical and experimental bases of each of the statements which they had, perhaps, taken for granted in their first course.

In addition to the usual subjects discussed in elementary textbooks on physical chemistry there are interesting chapters entitled: "Modern Theories of Electrolytes," "Radiations and Spectra," "The Nucleus," "Arrangement of External Electrons," and "The Electronic Theory of Valence." Each chapter is provided with a set of problems and exercises as well as a bibliography for outside study.

There can be little doubt that this book will fill the need for a text sufficiently advanced to interest students who have already acquired an elementary knowledge of chemistry, yet it is not too specialized and intricate to discourage them.

D. HARKER

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth Edition. System-Number 36, **Gallium.** Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany, 1936. 100 pp. 17 × 25 cm. Price, RM. 13.87.

This relatively slender volume, entitled "Gallium," discusses the free element itself and its compounds with the elements of smaller "System-Number"; *i. e.*, with the nonmetals, with the metals in the preceding group of the periodic table and with aluminum. The literature of the subject has been covered up to October 1, 1936, so that the important recent work of Goldschmidt and Peters and of I. and W. Noddack on the occurrence and that of Kraus and his collaborators on the preparation, of gallium are included. Indeed a surprisingly large fraction of all the data given in this book is of recent date, presumably because of late gallium and gallium compounds have become more easily available.

ARTHUR B. LAMB

Laboratory Methods of Organic Chemistry. By L. GATTERMANN. Completely revised by Heinrich Wieland. Translated from the Twenty-fourth German Edition by W. McCartney, Ph.D., A. I. C. The Macmillan Company, 60 Fifth Avenue, New York, 1937. xvi + 435 pp. 59 figs. 15.5 × 22.5 cm. Price, $4.50.

Gattermann–Wieland's Laboratory Manual is too well known to require a detailed description.

This edition has been revised in several very important parts. Perhaps the most significant change is the abandonment of all macro methods of analysis, and their replacement by semi-micro ("meso-analytical") procedures which require the use of only 20–30 mg. of sample.

There have also been some changes made in the list of experiments, with the omission of some and the addition of others which are of greater current interest. The new experiments include the preparation of a platinum oxide catalyst for reductions, the ozonization of cyclohexene to give adipic aldehyde and the separation of chlorophyll-*a* and chlorophyll-*b* by the method of chromatographic adsorption. Improved directions for the preparation of diazomethane and octaacetylcellobiose are given.

Space has been given to a short discussion of the Wolff–Kishner reduction and selenium oxide oxidations, and the sections on carbohydrates, porphyrins and chlorophyll, and sterols have been revised to cover recent developments. The pyrones, anthocyanins and oxonium salts are treated in this edition for the first time.

The improvement in indexing should be especially commended. This change has greatly increased the usefulness of this well-known laboratory manual. The new Gattermann–Wieland can be highly recommended to all organic chemists.

C. S. MARVEL

The Scientific Principles of Plant Protection, with Special Reference to Chemical Control. By HUBERT MARTIN, D.Sc., A.R.C.S., F.I.C. Longmans, Green and Company, 114 Fifth Avenue, New York, N. Y., 1936. xii + 379 pp. 14.5 × 22 cm. Price, $8.00.

Since the appearance of the first edition of this book, entomologists, plant pathologists and chemists have been so active in this field that in preparing the second edition, Dr. Martin has found it necessary to rewrite and reset all but the introductory chapter. The present edition gives an excellent up-to-date summary of the scientific literature on the control of insects and plant diseases, with many citations of the literature enabling the reader to go more deeply into any subject in which he is interested. It offers biological information to the chemist and chemical facts to the applied biologist.

Phases of control other than chemical are discussed. Among these are plant resistance, effects of fertilizers, biological control, traps, and the elimination of infection centers or vectors. A chapter is devoted to spreaders, stickers, protective colloids, and dispersing and emulsifying agents. This book should prove of value in clearing up confusing points in recent developments such as a difference between sulfated and sulfonated spreaders. A chapter on the measurement of toxicity and the relationship of chemical constitution to toxic action is of particular interest.

The work is not intended to give definite formulas, but to indicate broadly the field of usefulness of different methods of control and give the principles underlying these methods.

Various commercial products are mentioned and, where possible, the active ingredients are given. The author errs in stating that the calcium cyanide in Cyanogas is manufactured from liquid hydrocyanic acid and calcium carbide. The calcium cyanide in Cyanogas is made from calcium cyanamide, and the calcium cyanide resulting from the reaction of liquid hydrocyanic acid and calcium carbide is sold under the trade name of Calcid. The patent literature which represents much of the research work of commercial firms and which may suggest ideas to all workers in this field has not been covered. It is hoped that in a future edition the author may be able to cover the patent literature dealing with pest control as well as he has the scientific literature in the present edition.

This book should prove of great value to the mycologist, entomologist and chemist working in the field of pest control.

WILLIAM MOORE

Die Fermente und ihre Wirkungen. (Enzymes and their Action.) Supplement. Lieferung 5 (Bd. I Specieller Teil: Haupt-teil XII). By Prof. CARL OPPENHEIMER with the collaboration of Dr. W. ROMAN. W. Junk Verlag, Scheveningsche Weg 74, The Hague, Holland, 1936. 140 pp. 5 figures. 20.5 × 28 cm. Price, Fl. 10.

Lieferung (Installment) 5 is the fifth number in a series of separate supplements, the purpose of which, as stated in the reviews of the previous numbers [THIS JOURNAL, **58**, 538, 2344 (1936)] is to bring up to date the vast amount of information that has been accumulating in the field of enzyme chemistry during the past ten years since the publication of the original main treatise.

The present installment is devoted to the chemistry of the proteinases and various types of peptidases. Not only is the more recent information found in the chemical literature discussed, but considerable space has been devoted to recent studies on the constitution of proteins. About half of the number is given over to the chemistry of the peptidases, their methods of preparation and differentiation, and to a discussion of their properties such as stability, optimum pH, specificity, behavior on adsorption, sensitivity toward foreign substances, etc.

J. M. NELSON

The Nature of Water—Heavy Water. (In russian.) By E. KH. FRITSMAN. ONTI—Khimteoret, Leningrad, U. S. S. R., 1935. 314 pp. 15 × 22 cm. Price, bound cloth, rubles 7.00.

This monograph is one of the first attempts toward a broad discussion on the nature of water from the inorganic point of view. The first 106 pages are devoted to a discussion of the earlier literature on the properties and structure of water and of ice. Two pages are given to the ortho and para modifications of water, and the remainder of the 155 pages of the discussion of fundamental investigation is devoted to heavy water. In the section outlining special investigations, pages 162–206 relate to X-rays, Raman, and ultra-red analysis of water; pages 207–209 to ortho and para hydrogen. The remainder of the book is a review of important investigations relating to deuterium and deuterium oxide. Two pages are devoted to tritium and two to the heavy isotopes of oxygen. The author gives 699 references, about 260 of them relating to work done on heavy water. The reviewer has in his files approximately 1200 titles relating to heavy isotopes of hydrogen and oxygen through 1934. This work is a well written and valuable contribution in a field of wide present interest.

MERLE RANDALL

Thermodynamics of Chemical Reactions and Their Application to Inorganic Technology. By A. F. KAPUSTINSKII, Professor of Physical Chemistry, All-Union Scientific Research Institute of Economic Mineralogy, ONTI, Moscow, U. S. S. R., 1935, 2d edition in Russian. 303 pp. 15 × 22 cm. Price, bound cloth, rubles 5.00.

This book presents a short course in general physical chemistry with emphasis on thermodynamics for students and engineers. Chapters 1 and 2 give a brief elementary outline of the gas laws; Chapter 3, heat capacity including quantum theory; Chapters 4 and 5, first law of thermodynamics and thermochemistry; Chapter 6, liquefied gases; Chapter 7, second law and entropy; Chapter 8, vaporization; Chapter 9, theory of solutions; Chapter 10, phase rule; Chapter 11, chemical equilibrium; Chapter 12, free energy; Chapter 13, third law; Chapter 14, technical reversible reactions. There follows 35 pages of tables of thermodynamic functions and 198 selected equations are brought together in a final table. The American reader will find some difficulty in following the author owing to inconsistencies in terminology. The author recognizing the necessity of a uniform and consistent system of symbols has added his own system in a table summarizing several current systems. At the same time he does not invariably follow his chosen system. This is unfortunate, for otherwise the book appears to be well thought out and well written.

MERLE RANDALL

The Biochemistry of the Lipids. By HENRY B. BULL, Ph.D., Assistant Professor of Physiological Chemistry, Northwestern University Medical School. John Wiley & Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1937. ix + 169 pp. 63 figs. 15.5 × 23.5 cm. Price, $2.75.

This work was first published as a mimeographed book by the Burgess Publishing Company in 1935.[1] Through a happy thought of the author, the subject matter has been rearranged, rewritten and in some cases notably increased, with the result that he has succeeded in the production of a readable up-to-date textbook. As stated in the preface, its object is to give the graduate student in biochemistry an insight into the chemistry and physiology of the lipids. The book contains nine chapters, the titles of which are "The Fatty Acids," "The Soaps," "Alcohols, Waxes, and Hydrocarbons," "The Sterols and Related Compounds," "Fats and Oils," "The Phospholipids," "Cerebrosides," "Carbohydrate Esters of the Higher Fatty Acids" and "Emulsions." Although the treatment of the subject matter for the most part, as would be expected from the size of the volume, is much condensed, it will, with few exceptions, be found satisfactory. In all cases, however, adequate references are given. Also, the author has called attention several times to useful reviews covering a given subject which will prove helpful.

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(1) See Jamieson, THIS JOURNAL, **58**, 184 (1936).

G. S. JAMIESON

BOOKS RECEIVED

February 15, 1937–March 15, 1937

EMIL ABDERHALDEN, Editor. "Handbuch der biologischen Arbeitsmethoden. Abt. I, Teil 11, Heft 7." "Methoden zur Erforschung der Konstitution von Kohlenhydraten," by Percy Brigl and Hans Grüner. "Pektin," by Felix Ehrlich. Verlag Urban und Schwarzenberg, Friedrichstrasse 105 B, Berlin NW 7, Germany. 298 pp. RM. 16.50.

HERMAN T. BRISCOE. "An Introduction to College Chemistry." Houghton, Mifflin Company, 2 Park St., Boston, Mass. 653 pp. $3.00.

HENRY B. BULL. "The Biochemistry of the Lipids." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 170 pp. $2.75.

L. F. FIESER, Editor. "Organic Syntheses. Vol. XVII." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 112 pp. $1.75.

LEICESTER F. HAMILTON AND STEPHEN G. SIMPSON. "Talbot's Quantitative Chemical Analysis." Eighth edition. The Macmillan Company, 60 Fifth Ave., New York, N. Y. 297 pp. $2.50.

HANS HOHN. "Chemische Analysen mit dem Polarographen." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 102 pp. RM. 7.50.

E. RABALD, Editor. "Dechema Werkstoffblätter. Kurzreferate über Werkstofffragen in der chemischen Technik aus dem Schrifttum des in- und Auslandes." Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 104 pp. RM. 10.

J. SIVADJIAN. "Les Vitamines et les Hormones." Gauthier-Villars, Éditeur, 55 Quai des Grands-Augustins, Paris, France. 80 pp.

"Index to A. S. T. M. Standards and Tentative Standards." American Society for Testing Materials, 260 South Broad St., Philadelphia, Pa. 120 pp.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BROOKLYN COLLEGE OF PHARMACY]

Ternary Systems of Urea and Acids. IV. Urea, Citric Acid and Water. V. Urea, Acetic Acid and Water. VI. Urea, Tartaric Acid and Water

BY LAWRENCE H. DALMAN

In a previous publication[1] dealing with a phase rule study of the solubility relations of aqueous solutions of urea and acids, solubility measurements were reported for the three ternary systems of urea with nitric, sulfuric and oxalic acids. The existence of one or more double compounds was established in each system.

The present investigation is a continuation of this study and presents the results obtained in the determination of the three ternary systems consisting of urea, water and each of the following: citric, acetic and tartaric acids.

Materials

Urea.—The urea used was Mallinckrodt "Analytical Reagent." After recrystallization, analyses by the standard urease method[2] showed an average urea content of 99.8%.

Acetic Acid.—Merck C. P. acid was purified by freezing and preserved in a well-stoppered container. Titration with standard alkali indicated that it was 99.8% pure.

Citric and Tartaric Acids.—The anhydrous citric and *d*-tartaric acids were presented by Charles Pfizer and Company. Both of these acids were dried and stored over sulfuric acid. Titration against sodium hydroxide showed that the citric and tartaric acids averaged 99.9% and 99.8% of their theoretical values, respectively.

Standard Sodium Hydroxide.—This solution was prepared and used according to accepted standards. It was protected against dust, etc., and restandardized at regular intervals.

Procedure.—The description of the apparatus and the method of analysis of the saturated solutions has already been presented in a previous publication.[1] After the original complexes had been rotated to equilibrium at constant temperature, samples were withdrawn for the determination of acid by titration with alkali using phenolphthalein as indicator. Measurements for urea were made by the action of urease obtained from jack bean flour. The corresponding amount of ammonia liberated was taken up by hydrochloric acid and the excess acid titrated against alkali. Water was determined by difference.

This method for determining urea was used in the citric and tartaric acid systems with good results but proved unsatisfactory in the acetic acid system. The high values obtained for urea appear to be due to the fact that acetic acid is lost during the process of aeration for the removal of carbon dioxide. However, this easy volatility of acetic acid suggested an alternate method for the determination of urea which gave satisfactory results. A few cc. of the saturated solution was pipetted into a weighed porcelain crucible and evaporated to dryness in an oven maintained at 50–55°. The residue of urea was then dried to constant weight over sulfuric acid. By this method urea could be measured with an accuracy well within the limit of the urease method.

The composition of the original complexes and the solubility data obtained from the analyses of the saturated solutions have been expressed in weight per cent. and assembled in Tables I–III. The compositions of the solutions at the isothermally invariant points are the average of two or more closely agreeing results and not that of a single determination as the appearance of the isotherm would seem to indicate. In the last column are indicated the saturating solid phases which in the interest of economy of space have been abbreviated as follows: Ur for urea; C for $H_3C_6H_5O_7$; Ur·C for $CO(NH_2)_2 \cdot H_3C_6H_5O_7$; $Ur_2 \cdot C$ for $[Co(NH_2)_2]_2 \cdot H_3C_6H_5O_7$; $Ur_4 \cdot C$ for $[CO(NH_2)_2]_4 \cdot H_3C_6H_5O_7$; HAc for $HC_2H_3O_2$; $Ur \cdot AC_2$ for $CO(NH_2)_2 \cdot 2HC_2H_3O_2$; T for $H_2C_4H_4O_6$; $Ur_2 \cdot T$ for $[CO(NH_2)_2]_2 \cdot H_2C_4H_4O_6$; and $Ur \cdot T_2$ for $CO(NH_2)_2 \cdot 2H_2C_4H_4O_6$.

The identification of the various saturating solid phases was established by the method of extrapolation of the tie lines and confirmed by the analysis of the solids found in

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(1) Dalman, THIS JOURNAL, **56**, 549 (1934).

(2) Fox and Geldard, *Ind. Eng. Chem.*, **15**, 743 (1923).

TABLE I

UREA–CITRIC ACID–WATER

Original complex Wt., % Urea	Original complex Wt., % $H_3C_6H_5O_7$	Saturated soln. Wt., % Urea	Saturated soln. Wt., % $H_3C_6H_5O_7$	Solid phase
10°				
..	..	46.0	0.0	Ur
50.0	2.7	45.9	2.9	Ur
48.0	6.0	45.9	5.2	Ur + $Ur_4 \cdot C$
43.0	9.0	42.2	6.3	$Ur_4 \cdot C$
40.0	10.0	39.0	7.8	$Ur_4 \cdot C$
36.0	13.0	35.0	9.6	$Ur_4 \cdot C$ + $Ur_2 \cdot C$
30.0	13.0	29.5	10.4	$Ur_2 \cdot C$
25.0	14.0	24.6	12.1	$Ur_2 \cdot C$
20.0	20.0	18.8	14.3	$Ur_2 \cdot C$ + Ur·C
13.0	22.0	12.0	17.2	Ur·C
9.0	28.0	7.2	22.4	Ur·C
5.0	35.0	3.0	31.0	Ur·C
3.0	45.0	1.5	42.9	Ur·C
3.0	51.0	1.2	48.7	Ur·C
2.0	56.0	1.0	54.0	Ur·C + C
..	..	..	54.0	C
25°				
..	..	54.5	0.0	Ur
57.0	5.0	53.6	5.4	Ur
55.0	12.0	52.5	10.5	Ur + $Ur_4 \cdot C$
50.0	15.0	49.4	12.5	$Ur_4 \cdot C$
47.0	18.0	46.2	15.0	$Ur_4 \cdot C$
44.0	21.0	43.0	17.8	$Ur_4 \cdot C$ + $Ur_2 \cdot C$
38.0	22.0	38.0	19.3	$Ur_2 \cdot C$
33.0	24.0	32.5	21.7	$Ur_2 \cdot C$
28.5	27.5	28.2	23.8	$Ur_2 \cdot C$ + Ur·C
23.0	27.0	22.9	24.0	Ur·C
18.0	28.0	17.6	24.4	Ur·C
13.0	31.0	12.1	27.0	Ur·C
8.0	39.0	6.1	34.6	Ur·C
6.0	45.0	4.0	41.6	Ur·C
5.0	55.0	2.4	51.7	Ur·C
3.0	65.0	1.4	62.2	Ur·C + C
..	..	..	62.1	C
40°				
..	..	62.3	0.0	Ur
63.0	6.0	60.2	6.5	Ur
61.0	11.0	58.5	11.7	Ur
59.0	18.0	56.6	17.7	Ur + $Ur_4 \cdot C$
53.0	22.0	52.8	20.4	$Ur_4 \cdot C$
50.0	25.0	49.7	23.7	$Ur_4 \cdot C$
47.0	29.0	46.7	27.0	$Ur_4 \cdot C$ + $Ur_2 \cdot C$
43.0	30.0	43.2	28.7	$Ur_2 \cdot C$
40.0	32.0	40.1	30.3	$Ur_2 \cdot C$
36.5	36.0	37.0	32.1	$Ur_2 \cdot C$ + Ur·C
29.6	36.0	30.0	32.4	Ur·C
22.0	38.0	21.7	34.1	Ur·C
13.0	42.0	12.1	39.4	Ur·C
7.0	50.0	5.7	48.1	Ur·C
5.0	58.0	3.0	56.0	Ur·C
4.0	65.0	2.3	64.0	Ur·C
2.5	70.5	1.8	69.0	Ur·C + C
..	..	..	68.6	C

TABLE II

UREA–ACETIC ACID–WATER

Original complex Wt., % Urea	Original complex Wt., % $HC_2H_3O_2$	Saturated solution Wt., % Urea	Saturated solution Wt., % $HC_2H_3O_2$	Solid phase
10°				
..	..	46.0	0.0	Ur
48.0	7.0	45.9	7.3	Ur
47.0	14.0	45.5	14.4	Ur
47.0	21.0	44.8	21.8	Ur
46.0	28.0	43.6	29.3	Ur
45.0	35.0	42.3	36.7	Ur
43.0	42.0	41.7	40.7	Ur + $Ur \cdot Ac_2$
36.0	47.0	36.4	44.0	$Ur \cdot Ac_2$
27.0	55.0	25.8	52.9	$Ur \cdot Ac_2$
19.0	65.0	17.2	64.7	$Ur \cdot Ac_2$
14.0	75.0	12.3	75.6	$Ur \cdot Ac_2$
10.0	85.0	8.5	86.0	$Ur \cdot Ac_2$
10.0	88.0	7.0	90.5	$Ur \cdot Ac_2$
7.0	92.0	6.5	91.8	$Ur \cdot Ac_2$ + HAc
2.0	95.0	2.5	94.1	HAc
4.0	96.0	4.4	95.6	HAc
25°				
..	..	54.5	0.0	Ur
55.0	10.0	52.7	10.4	Ur
53.0	19.0	50.8	19.8	Ur
51.0	29.0	48.0	30.7	Ur
50.0	38.0	45.3	41.5	Ur
43.0	50.0	42.6	50.2	Ur + $Ur \cdot Ac_2$
36.5	56.0	37.0	54.4	$Ur \cdot Ac_2$
31.0	61.0	30.5	59.9	$Ur \cdot Ac_2$
24.0	69.0	22.8	69.3	$Ur \cdot Ac_2$
19.0	77.0	17.1	78.4	$Ur \cdot Ac_2$
14.0	85.7	11.2	88.5	$Ur \cdot Ac_2$
40°				
..	..	62.3	0.0	Ur
64.0	9.0	59.6	10.2	Ur
59.0	19.0	56.6	20.1	Ur
56.0	29.0	52.6	31.3	Ur
54.0	37.0	49.0	40.9	Ur
50.0	47.0	44.8	51.8	Ur
45.0	55.0	43.1	56.7	Ur
39.0	61.0	39.3	60.6	$Ur \cdot Ac_2$
37.0	63.0	37.0	62.7	$Ur \cdot Ac_2$
35.0	65.0	35.5	64.2	$Ur \cdot Ac_2$
33.3	66.7	33.2	66.3	$Ur \cdot Ac_2$
31.0	69.0	29.7	69.9	$Ur \cdot Ac_2$
28.0	72.0	27.0	72.8	$Ur \cdot Ac_2$

the sample tubes or of crystals grown by isothermal evaporation of solutions calculated to precipitate the desired solid phase. In either case the solid was separated from the saturated solution by means of a Gooch crucible and well centrifuged before analysis.

Results

The solubility of citric acid was measured by titration with approximately tenth normal sodium hydroxide using phenolphthalein as indicator. A survey of the literature for existing data with

TABLE III

UREA–TARTARIC ACID–WATER

Original complex Wt., % Urea	Original complex Wt., % $H_2C_4H_4O_6$	Saturated solution Wt., % Urea	Saturated solution Wt., % $H_2C_4H_4O_6$	Solid phase
		10°		
..	..	46.0	0.0	Ur
49.0	7.0	46.0	8.4	Ur
49.0	15.0	46.0	15.8	Ur
49.0	23.0	46.0	24.3	Ur
48.0	34.0	46.0	32.8	$Ur + Ur_2{\cdot}T$
41.0	38.0	40.6	36.1	$Ur_2{\cdot}T$
37.0	42.0	35.8	40.0	$Ur_2{\cdot}T$
34.0	45.0	32.3	43.4	$Ur_2{\cdot}T$
30.0	48.0	30.0	46.2	$Ur_2{\cdot}T + Ur{\cdot}T_2$
25.0	48.0	25.5	45.9	$Ur{\cdot}T_2$
20.0	49.0	20.3	45.9	$Ur{\cdot}T_2$
15.0	50.0	14.6	46.3	$Ur{\cdot}T_2$
10.0	51.0	9.3	48.2	$Ur{\cdot}T_2$
6.0	54.0	5.1	51.7	$Ur{\cdot}T_2$
5.0	55.0	4.6	54.3	$Ur{\cdot}T_2$
5.0	58.0	4.7	55.9	$Ur{\cdot}T_2 + T$
3.0	57.0	3.1	55.5	T
..	..	..	54.5	T
		25°		
..	..	54.5	0.0	Ur
57.0	8.0	53.2	8.7	Ur
56.0	16.0	51.8	17.5	Ur
55.0	25.0	50.3	27.7	Ur
51.0	36.0	49.0	35.9	$Ur + Ur_2{\cdot}T$
44.0	41.0	43.9	39.6	$Ur_2{\cdot}T$
39.0	46.0	38.0	44.4	$Ur_2{\cdot}T$
33.5	50.5	33.5	48.8	$Ur_2{\cdot}T + Ur{\cdot}T_2$
25.0	52.0	25.6	49.7	$Ur{\cdot}T_2$
20.0	53.0	20.3	50.5	$Ur{\cdot}T_2$
15.0	55.0	14.7	51.6	$Ur{\cdot}T_2$
9.0	57.0	8.4	54.6	$Ur{\cdot}T_2$
7.0	60.0	6.0	56.6	$Ur{\cdot}T_2$
5.5	61.0	5.0	59.1	$Ur{\cdot}T_2 + T$
3.0	61.0	3.2	58.8	T
..	..	..	58.5	T

which to compare the data obtained showed but a single reference, namely, that of Seidell[3] whose value given only at 25° was reported to be 61.71%. This compares favorably with 62.08% found in this investigation (average of four determinations).

The solubility of tartaric acid measured by the same method at 25° was found to be 58.51% (average of five determinations). Seidell's figure for the corresponding solubility is given as 57.9%, while Leidie[4] reported 59.79%. At 10° the solubility of Leidie is likewise about 1% higher than the value reported here in Table III.

Since these solubilities were measured by the same method the lack of agreement appears to be due to the quality of the acids used in the investigation. In view of this fact, a systematic determination of the solubility of carefully purified citric and tartaric acids has been undertaken in this Laboratory.

IV. Urea, Citric Acid and Water

This system was studied at 10, 25 and 40°; solubility data are shown in Table I and graphed in Fig. 1. The isotherm at 40°, which is given in complete detail, consists of five solubility curves indicating the existence of five solid phases including three double salts. Reading from left to right, these solid phases are: urea for solutions between points a and b; tetraurea citrate for b–c; diurea citrate for c–d; monourea citrate for d–e; and anhydrous citric acid for e–f.

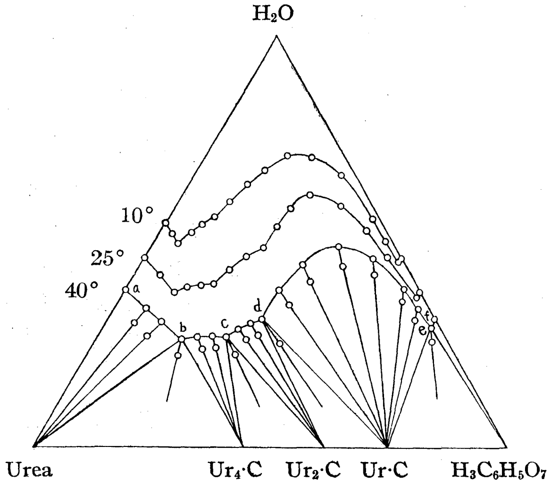

Fig. 1.—10, 25 and 40° isotherms.

The isotherms at 10 and 25° also contain five solubility curves and differ from that at 40° only in that the solid phase corresponding to the curve e–f is citric acid monohydrate instead of the anhydrous acid. This curve, of course, disappears from the system at the temperature of the transition of the monohydrate to the anhydrous acid which has been found to be 35.80°.

The Quintuple Point.—It is evident from these considerations that the curve for anhydrous citric acid originates between 25 and 40° and at the isothermally invariant point e when the system already contains vapor, solution and two solid phases. The introduction of fifth phase results in an invariant system possessing no degrees of freedom. By means of cooling curves this invariant temperature was found to be 33.73°. The composition of the saturated solution at the quin-

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[3] Seidell, *Bull. No. 67, Hyg. Lab.*, 1910.

[4] Leidie, *Compt. rend.*, **95**, 87 (1887).

tuple point was not determined. Although the tie lines have been omitted from the 10 and 25° isotherms, their extrapolation to the proper solid phases has been found to be quite satisfactory.

Further, while not indicated, the curves a–b and d–e have been found to extend metastably into the area of the tetraurea citrate where they intersect to form a metastable isothermal invariant point.

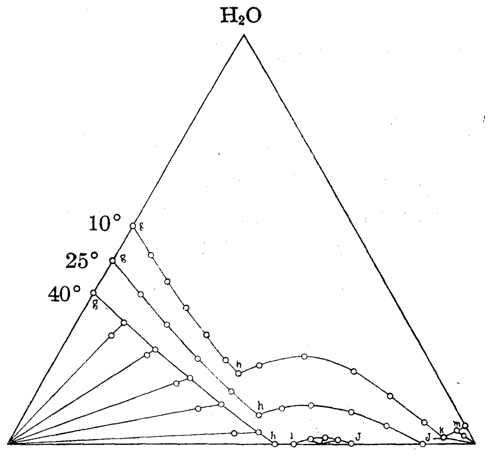

Fig. 2.—10, 25 and 40° isotherms.

It is possible to prepare the salts of monourea and diurea citrate in excellent purity since they form hard, well-defined crystals of considerable size which yield good analytical results.

	Calculated, %			Found, %		
	Urea	Acid	H_2O	Urea	Acid	H_2O
Ur·C	23.82	76.18	0.00	23.7	75.7	0.60
Ur$_2$·C	38.47	61.53	.00	38.1	61.0	.90

Both of these salts have been prepared and described by previous investigators; monourea citrate by Hlasiwetz[5] and diurea citrate by Loschmidt.[6]

The tetraurea citrate, on the contrary, separates slowly from well-cooled solutions, or by proper seeding forming small, lustrous flakes which fail to develop into sizable crystals even on prolonged agitation in the thermostat. After being filtered rapidly and centrifuged at 300 r. p. m., the salt still showed 6–7% of water. Since the salt shows incongruent solubility, its composition could not be determined by evaporating its solutions to dryness. However, the tie lines extrapolated to the composition of tetraurea citrate with suitable accuracy. Moreover, the analyses of the centrifuged wet residue fell satisfactorily on these tie lines and the salt is therefore reported as tetraurea citrate.

V. Urea, Acetic Acid and Water

This system was likewise investigated at 10, 25 and 40°; the experimental results are shown in Table II. The system has been found to produce only one double salt and this has been described by Du Toit.[7] The solubility curves are drawn in Fig. 2. Due to the high solubility of urea diacetate, the isotherms resemble those found in the sulfuric acid system.[1]

At 10° the isotherm consists of three intersecting curves which represent solutions in equilibrium with urea g–h, urea diacetate h–k, and solid acetic acid k–m. The latter curve is missing at 25°, and the curve for urea diacetate therefore terminates at the base line at the solubility of the double salt in pure acetic acid, j. The isotherm at 40° differs from those at 10 and 25° in that the curves for urea and diacetate no longer intersect but exist as two separate curves. This follows as a natural consequence of the downward movement of the isotherm with rising temperatures. Point h now represents the solubility of urea in acetic acid, while i and j denote the limits of solubility of urea diacetate in acetic acid. The curve for this salt has been enlarged somewhat in order to render a clearer picture of its scope.

While no tie lines have been drawn for the double salt, their extrapolation leaves little doubt as to its identity. On analysis it was found to contain: calcd. for $CO(NH_2)_2 \cdot 2HC_2H_3O_2$; urea, 33.34; acid, 66.66. Found: urea, 32.9; acid, 65.6; water, 1.5%.

The melting point of urea diacetate has been reported to be about 35° by Du Toit.[7] Since this solid phase was found to be stable at 40° it was decided to repeat this melting point determination. The results showed that the double salt melts slowly at 35° and more rapidly as the temperature is increased to 41° when the change is quite sudden. Inasmuch as this salt decomposes rapidly on exposure to air through the evaporation of acetic acid, the same decomposition undoubtedly occurs in the open capillary tube, and thus interferes with the melting point determination. This difficulty was eliminated satisfactorily in a closed tube in the following manner. A regular glass-stoppered solubility

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(5) Hlasiwetz, *J. prakt. Chem.*, **69**, 104 (1856).

(6) Loschmidt, *Jahresb. Chem.*, 658 (1865).

(7) Du Toit, *Verslag. Wetenschschappen*, **22**, 573 (1913).

tube was loaded with urea and acetic acid in the proportions in which they occur in the salt. The contents were warmed until complete solution occurred and then cooled until only a small amount of crystals had formed. The tube was rotated in the bath and the temperature adjusted so that the quantity of crystals appeared to remain constant over a period of a few hours. This temperature was found to lie between 41.25 and 41.30°. However, in view of small impurities present in the urea and acid, the melting point of urea diacetate is reported to be 41.3°.

Above this temperature then the isotherm (providing no new phases enter the system) contains only the curve g–h which represents the solubility of urea ranging from pure water to pure acetic acid.

VI. Urea, Tartaric Acid and Water

In this system solubility measurements were made at 10 and 25°; these data are assembled in Table III. The isotherms which are drawn in Fig. 3 are very similar and consist of four curves which represent solutions in equilibrium with urea n–o, diurea tartrate o–p, urea ditartrate p–r and tartaric acid r–s. The solutions saturated with these double salts were found to be highly viscous.

Diurea tartrate, which has been prepared and described by Loschmidt,[6] was found to consist of rather soft crystals which gave the following results on analysis: calcd. for $U_2 \cdot T$: urea, 44.46; acid, 55.54. Found: urea, 43.4; acid, 54.5; water, 2.1%.

Urea ditartrate, which has been reported by Hlasiwetz,[5] crystallizes exceedingly slowly. As in the case of tetraurea citrate, this salt still contained about 11% of water after being centrifuged thoroughly. However, the analyses of wet residues fell satisfactorily on the tie lines extrapolating to the composition of a 1:2 double salt and its identification is therefore considered to be suitably established.

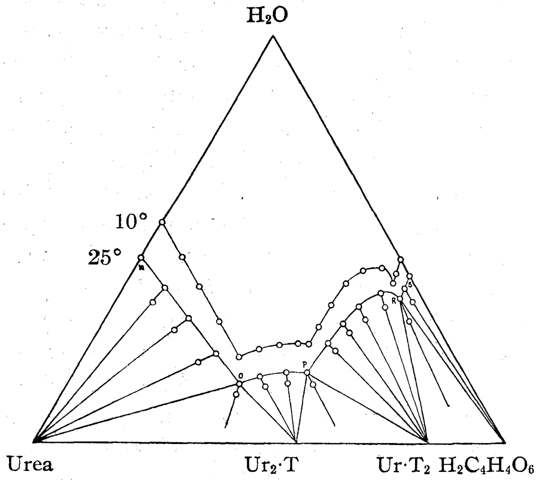

Fig. 3.—10 and 25° isotherms.

Summary

The solubility relationships in the systems urea–citric acid–water and urea–acetic acid–water have been studied at 10, 25 and 40°; the system urea–tartaric acid–water has been studied at 10 and 25°.

The following double salts were found to exist: tetraurea citrate, diurea citrate, monourea citrate, diurea tartrate, urea ditartrate and urea diacetate.

The urea diacetate has been found to exist only below 41.3°; citric acid monohydrate only below 35.80° and anhydrous citric acid only above 33.73°.

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

Hydrides of Boron. VII. Evidence of the Transitory Existence of Borine (BH_3): Borine Carbonyl and Borine Trimethylammine

BY ANTON B. BURG AND H. I. SCHLESINGER[1]

On account of its position in the periodic system and the composition of its most widely known compounds, boron has generally been regarded as a trivalent element; its hydrides therefore might have been expected to have the "normal" formulas BH_3, B_2H_4, B_3H_5, etc. Actually, however, the simplest known hydride of boron is diborane (B_2H_6), a substance whose formula is characteristic of some compounds of tetravalent elements. This formula has not as yet been explained by any generally accepted rules of molecular structure, nor has there been any obvious reason for the failure of all previous attempts to find evidence for the existence (whether stable or transitory) of the "normal" hydrides, or borines. It is therefore of interest to discover what conditions may be sufficient for the existence of such borines and their derivatives.

Progress in this direction is now given new impetus by the discovery of a gaseous compound having the molecular formula BH_3CO. This new substance is produced by the treatment of diborane with carbon monoxide (present in great excess), which acts according to the equation $B_2H_6 + 2CO \rightleftharpoons 2BH_3CO$. The reaction reaches equilibrium rapidly at 100°; at room temperature, the reverse reaction is slow enough to permit the isolation and study of the product. The molecular formula was established by observing the volumes of diborane and carbon monoxide produced by the decomposition of a known volume of the gas; the result was checked by hydrolytic analysis, and by the determination of the vapor density.

The initial rate of decomposition of BH_3CO at room temperature is relatively high, but decreases very rapidly, long before the final equilibrium is reached. The inhibiting agent is the carbon monoxide produced by the reaction; the other product, diborane, has no appreciable effect upon the rate in the early stages of the process. These observations suggest that the reaction occurs in two steps, the first of which results in the transitory existence of the hitherto unknown compound borine, according to the equation $BH_3CO \rightleftharpoons BH_3 + CO$. This presumably rapid and easily reversible reaction is carried forward by the removal of borine, as a result of the almost irreversible secondary reaction $2BH_3 \leftrightarrows B_2H_6$,[2] a reaction whose rate determines the rate of the entire process in its early stages. As the concentration of carbon monoxide increases, during the course of the whole reaction, its increasing effectiveness in reversing the primary reaction makes the borine less and less available for the secondary reaction, whose rate therefore decreases rapidly.

This interpretation implies the transitory existence of molecules of borine, and at the same time suggests that its isolation is not feasible. Since we are, therefore, unable to present this most direct proof of its existence, we offer the following additional indirect evidence. Any substance capable of uniting with molecules of borine to form a compound more stable than BH_3CO, should displace carbon monoxide from BH_3CO. Ammonia might have been expected to react in this manner, for it is known to form many stable addition products by reaction with "normal" boron compounds, but the actual reaction of ammonia with BH_3CO does not liberate carbon monoxide. Instead, there appears a solid material, stable at room temperature, having the empirical composition represented by the formula $BH_3CO(NH_3)_2$.[3] Considering that this result might be due to the labile character of hydrogen in ammonia, we tried the effect of trimethylamine upon BH_3CO and found that it displaces the carbon monoxide rapidly and completely at ordinary temperature, according to the equation, $BH_3CO + (CH_3)_3N \longrightarrow (CH_3)_3NBH_3$

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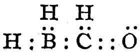
[1] Presented in condensed form at the Chicago Meeting of the National Academy of Sciences, Nov. 17, 1936.

[2] Our reason for supposing this reaction to be nearly irreversible is based upon an experiment by Stock and Kusz, *Ber.*, **56B**, 799 (1923), in which a sample of diborane was heated as high as 155°, without showing the slightest evidence of the formation of borine. Our only evidence that the reaction is reversible at all, is the fact that BH_3CO actually is formed from diborane and carbon monoxide.

[3] This material is in need of further investigation. It reacts with sodium in liquid ammonia to produce the quantity of hydrogen corresponding to two ammonium ions per molecule of BH_3CO, and therefore appears to have the character of a dibasic acid. Nevertheless, it is not yet possible to decide whether it is a pure compound, or a mixture of substances formed by the decomposition of BH_3CO during its reaction with ammonia.

$+ CO$. This reaction is in agreement with our assumption of the transitory existence of borine. The high speed of this displacement seems to justify the conclusion that the reaction $BH_3CO \rightleftarrows BH_3 + CO$ is far more rapid than the association of borine to form diborane.[4]

The reactions here described support the assumption that BH_3CO has the structure of a "borine carbonyl," a compound in which borine and carbon monoxide are joined by a coördinate link consisting of electrons furnished by the carbon monoxide.[5] Another structure which might be considered is  $\mathrm{H}:\overset{\mathrm{H}}{\ddot{\mathrm{B}}}:\overset{\mathrm{H}}{\ddot{\mathrm{C}}}::\ddot{\mathrm{O}}:$, which is an aldehyde type. Aside from the difficulty that such a substance should not easily produce diborane and carbon monoxide, there is the positive objection that it would be expected to add diborane, as acetaldehyde and other organic compounds containing the $=C=O$ group have been found to do.[6] The absence of such a reaction makes the aldehyde structure highly improbable. Other alternative structures which might suggest themselves seem too unlikely for discussion.

The compound $(CH_3)_3NBH_3$, borine trimethyl*ammine*, is extraordinarily stable. During the determinations of molecular weight and vapor tensions, it was heated for hours at a time at temperatures as high as 125°, without showing the slightest sign of a change in physical properties.

The studies here presented are being continued along several major lines. One of these is the investigation of the behavior of the alkyl diboranes and some of the higher boranes with carbon monoxide and with trimethylamine. The methyl derivatives of diborane already have been found to react with carbon monoxide, but the result is a series of compounds far different from BH_3CO.[7] In addition to this program, we are searching for other compounds which, like carbon monoxide and trimethylamine, may unite with the borine molecule to form compounds capable of isolation and study. These lines of work should lead to a better understanding of the nature of the boron hydrides and of the numerous "addition compounds" which they seem to be capable of forming.

Experimental Part[8]

Preparation of Borine Carbonyl.—Comparison of the results of a number of preliminary experiments showed that the equilibrium represented by the equation $B_2H_6 + 2CO \rightleftarrows 2BH_3CO$ is closely approached in fifteen minutes at 90°, but that less severe heating is not adequate for the purpose. Longer heating, or the same duration at a higher temperature, leads to no improvement in the yield; on the contrary, the increased production of less volatile material[9] involves a loss. At room temperature the reaction is very slow: after three hours the yield was only 1% of that obtained from a parallel experiment in which equilibrium was attained at 100°.

This preliminary study was followed by experiments in which mixtures of diborane with high concentrations of carbon monoxide[10] were heated in bomb tubes. In each of these experiments, a known quantity of diborane, and then a much larger, measured volume of carbon monoxide were condensed into the bomb at $-210°$.[11] The bomb was sealed off, removed from the low temperature bath, and inverted just as the diborane melted, in order that the liquid running down might evaporate and mix thoroughly with the carbon monoxide. Adequate mixing was made still more certain by allowing the tube to remain for ten hours or longer at room temperature, before the reaction was carried on by a twenty-minute heating in a steam-bath. After the heating, the bomb was cooled to $-196°$, and the contents introduced into the vacuum apparatus by means of the vacuum tube opener. In two of these experiments, in which data for the calculation of the equilibrium constant were recorded, the first fraction of the carbon monoxide was analyzed for hydrogen by combustion. The diborane and the borine carbonyl were isolated with un-

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(4) The compound $(CH_3)_3NBH_3$ is also formed very easily by the action of trimethylamine upon diborane, even at temperatures as low as $-110°$. This reaction probably does not depend entirely upon the dissociation of diborane to free borine molecules at such a low temperature; it is more reasonable to suppose that the trimethylamine acts upon diborane directly. Similarly, trimethylamine may react directly with BH_3CO. On account of this possibility, the formation of $(CH_3)_3NBH_3$ is not in itself a clear proof of the free existence of borine.

(5) For the present purpose, we consider it unnecessary to decide whether the carbon atom or the oxygen atom is linked directly to boron. Our use of the term "carbonyl" is solely a matter of convenience.

(6) These results have not yet been published. We have found that diborane reacts rapidly with acetaldehyde to give diethoxyborine, with acetone to give a compound which seems to be diisopropoxyborine, and far more slowly with methyl formate to give dimethoxyborine. The aldehyde and ketone reactions are completed in ten minutes at room temperature.

(7) Experimental work of F. L. McKennon.

(8) The high vacuum methods used in this work have been described quite adequately in the papers of Stock and in earlier papers of this series. All volumes mentioned in this paper refer to gases at standard conditions.

(9) This material in itself is worthy of further study. Like borine carbonyl, it begins to decompose rapidly at room temperature, and this initial reaction is soon hindered by the carbon monoxide which it produces. Unlike BH_3CO, the material produces a white, non-volatile solid which turns brown when heated. These observations suggest a carbonyl of a boron hydride fragment heavier than BH_3.

(10) The diborane was prepared by our usual method [Schlesinger and Burg, THIS JOURNAL, **53**, 4321 (1931)]. The carbon monoxide was prepared *in vacuo* by the action of hot sulfuric acid upon formic acid, and purified by distillation from a tube at $-196°$ to a receiver at $-210°$ (liquid nitrogen, whose temperature had been lowered by pumping).

(11) The uncondensed carbon monoxide was removed by a Töpler pump and measured over mercury. The purity of the sample was checked by combustion of this remainder.

usual care,[12] and the purity of each was checked before the volume was measured. The conditions and results of the bomb tube experiments are shown in Table I. Comparison of the last experiment with the others, shows very clearly the value of a high concentration of carbon monoxide.

TABLE I

Conditions			Results				
Capacity of bomb, cc.	Volume of B_2H_6	Volume of CO	Volume of BH_3CO	Residual volume of B_2H_6	Residual volume of CO	Volume of H_2	Volume of less volatile material
93.0	73.7	297	36.3	49.0	258	5	2.7
87.3	82.4	305	38.6	54.4	263	6.5	3.4
61.5	70.7	670	77.8	24.9	(585)	...	...

All volumes in this table are expressed in cc.

The equilibrium constant for the reaction $B_2H_6 + 2CO \rightleftarrows 2BH_3CO$ may be calculated from the data of the first two experiments in Table I. Expressing the concentrations in terms of partial pressures (in mm.), we have from the first experiment

$$K = (P_{CO}^2 \times P_{B_2H_6})/P_{BH_3CO}^2 = 2.8 \times 10^4$$

The second experiment gave the result $K = 3.0 \times 10^4$. Neither result is to be regarded as very precise, because the side reactions, the possible lack of perfect mixing, the chance that equilibrium was not perfectly attained, and even some slight decomposition of the borine carbonyl during purification, all must be considered as sources of error. The tendency is toward high results; we therefore consider the lower value to be more dependable, and take it to represent a maximum value of the constant.

This result means that a sample of pure BH_3CO, having an initial pressure of 200 mm. at 100°, would be approximately 95% decomposed if brought to equilibrium at that temperature (secondary and side reactions neglected).

Physical Properties.—The uniformity of various samples of the new compound was indicated by the consistent checking of the vapor tension of 25.4 mm. at −111.8° (m. p. of carbon disulfide). As a further check on the uniformity of the material, the melting points of three separately purified samples were measured by the magnetic plunger method of Stock.[13] The three readings of the carbon tetrafluoride vapor tension thermometer were 382, 382 and 381 mm., corresponding to −137.0, −137.0 and -136.9_7°.

In addition to these tests, the vapor tensions at a number of different temperatures were measured, and the results found to be consistent with the Clapeyron equation. The rapid decomposition of the vapor made such measurements difficult, but it was possible, by rapid establishment of the thermal equilibrium, by very fast readings of the temperature and pressure, and by careful repurification between measurements, to obtain satisfactory check values. In order to establish equilibrium rapidly enough, it was necessary to choose samples so small that the thermal capacity of the liquid would be negligible. It was thus possible to obtain each reading within half a minute after warming the sample from −196°. The values, corrected for the expansion of mercury above 0°, are shown in Table II. The equation representing them is $\log_{10} p_{\text{mm.}} = 7.85 - (1040/T)$, from which we calculate the normal boiling point to be −64°, the heat of vaporization 4750 cal./mole, and the Trouton constant 23.0 cal./deg. mole. The high value of the Trouton constant suggests that the complete curve relating log p to $1/T$ would be slightly concave downward, and that the true boiling point may be one or two degrees higher.

TABLE II

$t°$	−137	−122	−121.2	−120.3	−112.8	−111.8	−103.5	−95.6	−87.5	−87.2	−78.8
$p_{\text{mm.}}$ (obsd.)	1.4	9.0	9.7	10.7	22.5	25.4	52.8	98.6	175	181	314
$p_{\text{mm.}}$ (calcd.)	1.6	9.3	10.0	11.1	23.0	25.4	51.9	98.2	177	180	316

Analyses and Molecular Weight.—The most direct evidence of the identity of the new compound came from a quantitative experiment on its decomposition.

The sample was allowed to stand at room temperature for an hour. The carbon monoxide was then removed (through a trap at −196°) by a Töpler pump, and collected over mercury in a gas-measuring tube. The material in the trap was warmed again to room temperature, and the process of decomposing the original substance, and removing the carbon monoxide, was repeated again and again until the mixture no longer gave off more than traces of carbon monoxide. The latter stages of the process were facilitated by heating the mixture to 50°.

A 23.9-cc. sample thus yielded 24.1 cc. of non-condensable gas, 10.4 cc. of diborane, 0.7 cc. of material less volatile than the original sample, and a residue of 0.5 cc. of the original substance. The non-condensable material was analyzed by combustion and found to consist of 22.2 cc. of carbon monoxide and 1.9 cc. of hydrogen. The hydrogen and the least volatile material were unavoidable results of the heating.

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(12) The material less volatile than borine carbonyl seemed to be trapped out completely at −120°; its elimination was made certain by passing the more volatile materials very slowly through a trap at −145°. Nearly all of the borine carbonyl condensed in pure condition at −155°, but the purification of the diborane required a very slow distillation through a U-tube at −165°. The fraction trapped out at that temperature required further separation.

(13) Stock, *Ber.*, **50**, 157 (1917).

TABLE III

Time, min.		0	0.5	1.5	2.5	3.5	4.5	5.5	6.5	7.5	10.5
Pressure, mm.		161.3	162.3	164.3	165.3	166.0	167.1	168.2	168.8	169.3	170.3
% decomposed[a]		0	1.2	3.7	5.0	5.8	7.2	8.6	9.3	10.0	11.2
Time	17.5	27.5	57.5	87.5	118	148	210	270	360	450	520
Pressure	171.2	172.4	174.4	176.0	177.2	178.0	180.2	181.8	183.5	184.5	186.0
% decomp.	12.3	13.8	16.2	18.2	19.7	20.7	23.4	25.4	27.5	28.8	30.6

[a] The percentage decomposed at each point was calculated by dividing the total increment of pressure (multiplied by 100) by one-half the initial pressure.

Neglecting these side-reaction products, the results give the empirical molecular formula $B_{0.89}H_{2.82}(CO)_{0.96}$. The neglected material could easily represent the difference between this empirical result and the rounded formula, BH_3CO. At the same time, there could be some doubt that the observed quantities represented all of the material in the original sample, for non-volatile products could have remained unobserved in the form of a thin film on the glass walls of the container. The results therefore were supplemented by a determination of the molecular weight.

The molecular weight was calculated from the vapor density, determined in the usual manner. The sample (20.0 cc.) had a weight of 37.5 mg.: the molecular weight therefore was 42.0 (theoretical for BH_3CO, 41.85; considering the instability of the substance, such close agreement probably was fortuitous).

The formula BH_3CO was checked more definitely by the complete hydrolysis of a measured sample of the pure compound, followed by the combustion of the non-condensable gases and the titration of the boric acid. A 15.95-cc. sample, which was inclosed in a 250-cc. bulb with a liberal excess of water and heated for three hours at 100°,[14] produced 47.3 cc. of hydrogen, 15.7 cc. of carbon monoxide, and 16.0 "cc."[15] of boric acid. These results agree well enough with the expected equation $BH_3CO + 3HOH \longrightarrow B(OH)_3 + 3H_2 + CO$, to remove any doubt concerning the molecular formula of the compound.

The Rate of Decomposition.—The change in the rate of the reaction $2BH_3CO \longrightarrow 2CO + B_2H_6$, at room temperature, was studied by observing the relation of the total pressure to the time. The reaction evidently was not simple, for there occurred 8% decomposition during the first five minutes, 11% in ten minutes, 13% by the end of twenty minutes and only 13.8% at the half-hour point: a further eight-hour period was required to reach 30% decomposition. The detailed results are shown numerically in Table III, which records the progress of the decomposition of a 17.8-cc. sample at 23°, and graphically by curve I in Fig. 1.

The small rate of change toward the end of this experiment was shown not to be due to a close approach to equilibrium, by the behavior of the mixture after it had been heated for four hours at 50–60°. This treatment caused the extent of decomposition to increase from 30.6 to 78%. Nevertheless, the decomposition continued after the resulting mixture had been cooled to 24°.

The cause of the rapid decrease in the velocity of decomposition was made clear by further observations of the pressures registered by the same sample, after the carbon monoxide (accumulated in the course of the experiment described above) had been removed by pumping through a trap at −196°. The materials condensed (6.8 cc. B_2H_6, 3.7 cc. BH_3CO, and a trace of less volatile material) were returned to the reaction tube. The results of observations at 24° are shown in Table IV, and as curve II in Fig. 1. The sharp change in the behavior of the sample, as a result of removing carbon monoxide, leaves but little doubt that carbon monoxide is the main cause of the rapid slowing of the rate of decomposition, for the new rate curve is much like the original.[16]

The effect of carbon monoxide was tested more

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(14) The use of such a large bulb, and the drastic heating, seemed to be necessary for complete hydrolysis, since a somewhat smaller sample, heated with water for half an hour at 100°, in a space of 17 cc., was only 92% hydrolyzed. Hydrolysis thus appears to be an indirect reaction, in which a product of the decomposition (borine or diborane) is the material reacting with water. The high concentration of carbon monoxide built up in the smaller tube would stabilize the BH_3CO to such a degree as to account for the observed difficulty of hydrolysis.

(15) The symbol "cc." is used to represent the standard gas volume equivalent to a substance determined by titration.

(16) The rate of decomposition was considerably higher at any point in the present experiment than at the corresponding point in the original experiment. The difference no doubt was due mainly to the fact that the smaller sample in the same space built up a far lower partial pressure of carbon monoxide.

TABLE IV

Time, min.	0	0.5	1.0	3.0	8.0	16	23
Pressure, mm.	104.5	105.5	106.0	107.0	108.3	109.0	109.5
% decomposed[a]	0	6	9	15	23	27	30
Time, min.	32	43	53	76	191	270	546
Pressure, mm.	110.0	110.3	110.5	111.0	112.8	113.5	114.5
% decomposed[a]	33	34.5	36	39	49	54	59.5

[a] The % decomposed was calculated by dividing the total increment of pressure (multiplied by 100) by half the estimated initial partial pressure of BH_3CO (that is, by 0.5 × 33.6). It may be that the decomposition of the trace of less volatile material contributed to the rise of pressure: if so, these calculated values might be high by as much as 10 units. This uncertainty has no effect upon our conclusions, for a suitable correction would not alter the character of the curve.

directly in an experiment in which borine carbonyl and carbon monoxide were allowed to mix by diffusion at −80° (during twelve hours), after which the mixture was suddenly warmed to room temperature. The relation of the total pressure to the time was then observed as before.

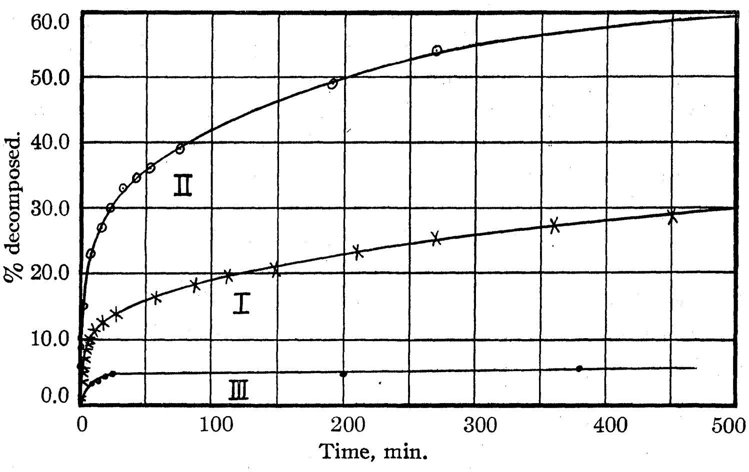

Fig. 1.

Table V shows the results obtained with such a mixture of 15.0 cc. BH_3CO and 22.2 cc. of carbon monoxide at 26°.

TABLE V

Time, min.	0	10	15	20	25	200	380
Pressure, mm.	320	322	322.3	322.7	322.8	323	323.5
Partial pressure of BH_3CO (calcd.)	120	116	115.4	114.6	114.2	114	113
% decomposition	0	3.3	3.8	4.5	4.8	5.0	5.8

At the end of this experiment, the diborane was isolated and measured as 0.4 cc., corresponding well with the 3.5 mm. increase of pressure. The rather rapid beginning of the decomposition probably is best explained by supposing that the mixing was not thorough enough for a perfect result.

Comparison of these results (curve III, Fig. 1) with those of the other rate experiments, fully confirms the conclusion that carbon monoxide is the inhibitor in the decomposition of borine carbonyl.

The Action of Ammonia upon Borine Carbonyl.—The original purpose in the treatment of borine carbonyl with ammonia was discussed in the introduction. The experimental details are as follows.

A pure sample of borine carbonyl (20.5 cc.) was treated with a large excess (114.1 cc.) of sodium-dried ammonia, at −124°. After an hour, the temperature was raised gradually to −80°, and the excess ammonia sublimed off into a trap at −196°. No trace of uncondensed gas was observed during this process. The solid residue now contained three moles of ammonia per mole of borine carbonyl originally used: this ratio was further decreased by warming the residue slowly to room temperature and condensing the ammonia liberated in the process. This second stage in the removal of ammonia was accompanied by the formation of 0.25 cc. of non-condensable gas, and a small sublimate of slightly volatile material. The solid residue in the original reaction tube now had an empirical formula approximating $(BH_3CO)_{0.9}(NH_3)_{2.07}$. It appeared to be fairly stable at room temperature.

In considering the possible ways in which ammonia might add to borine carbonyl, without liberating carbon monoxide, it seemed worth while to learn whether the product contained any ammonium ions. Accordingly, we tried the action of sodium upon a fresh sample of the material, dissolved in liquid ammonia.

The new sample was made from 14.0 cc. of borine carbonyl and a large, undetermined excess of ammonia. The solid was washed down to the bottom of the reaction tube by melting ammonia which had been condensed above it, and the solution was frozen during the introduction of 36.1 mg. of pure sodium (by a technique which blank tests had previously shown to be suitable for the purpose). When the solution was melted (allowing the sodium to enter the liquid phase at −77°), there occurred a very rapid reaction which produced one gram atom of hydrogen per gram molecule of borine carbonyl originally used. A secondary reaction produced a second gram atom of hy-

TABLE VI

Temperature, °C.	−77	−79	−77	−50	−49
Total time, min.	4	45	180	1560	3060
Total H_2, cc.	7.16	7.30	7.50	14.50	15.08
Ratio of H-atoms to BH_3CO used	1.02	1.04	1.04	2.07	2.16

drogen in the course of a day. The course of the whole reaction is shown in Table VI.

The excess over two atoms of hydrogen is properly to be attributed to amide formation.

The sodium reaction thus demonstrated that the product of addition of ammonia to borine carbonyl contains two ammonium ions per molecule of borine carbonyl. The question whether the material is a diammonium salt or a mixture of two salts, has not been decided.

Borine Trimethylammine

Preparation.—The reaction of trimethylamine with borine carbonyl appears to require temperatures as high as those at which the decomposition of the latter compound is observable. For example, there is no observable displacement of carbon monoxide by trimethylamine at −80°, but the reaction proceeds very rapidly at room temperature.

Thus 14.0 cc. of borine carbonyl and 25.0 cc. of trimethylamine, condensed into the tubulature of a reaction bulb (which was sealed while the reactants remained at −196°), and then warmed suddenly to room temperature, produced the solid material so rapidly that there was no further change after one minute. The reaction bulb was opened by a tube-opener, and the carbon monoxide was passed through a trap at −196°, by means of a Töpler pump, and measured as 14.2 cc. The residual trimethylamine was isolated by distillation through a trap at −80°, and measured as 10.8 cc.; the quantity which reacted hence was 14.2 cc., in perfect agreement with the quantity of carbon monoxide. The solid product therefore had the empirical composition $(CH_3)_{3x}(NBH_3)_x$, within the probable error.

Physical Properties and Molecular Weight.—The vapor tensions at various temperatures, and the total volumes of samples used in the determinations of the molecular weight, were measured by the aid of the device represented in Fig. 2. During such work, the sample contained in the bulb B registers its pressure upon the adjacent manometer, whose mercury levels are compared by means of a cathetometer. The complete immersion of the parts containing the sample makes it possible to work at elevated temperatures. In order to introduce or remove the sample, the mercury is lowered in the manometer to the point M, by applying a pump connection at P, and opening the ground-glass valve V.

The measurements so obtained for the vapor tensions of the solid product of the reaction of borine carbonyl and trimethylamine, were corrected for the varying density and vapor tension of mercury at different temperatures. The results are presented in Table VII. In the course of these measurements, the *melting point* was observed to lie between 94 and 94.5°.

TABLE VII

$t°$	23	27	34	39	51	60.3	69.5	77.6	82.7
$p_{mm.}$ (obsd.)	0.8	1.0	1.5	2.6	5.5	9.4	18.7	28.5	37.9
$p_{mm.}$ (calcd.)	0.7	1.0	1.6	2.4	5.5	10.1	17.8	28.4	37.8
$t°$	86.8	96.9	99.3	104.0	111.2	117.2	118.7	119.7	
p (obsd.)	47.8	76.5	84.7	101.7	130.0	159.8	166.0	171.8	
p (calcd.)	47.9	78.2	85.3	101.4	130.6	160.0	167.5	173.4	

The values of the vapor tension below the melting point led to the equation $\log_{10} p_{mm.} = 10.187 - 3061/T$. The values above the melting point gave the equation $\log_{10} p_{mm.} = 7.846 - 2202/T$. Eliminating log p from these equations and solving for T gives a calculated melting point of 94°, in close agreement with direct observation. The heat of vaporization below the melting point is calculated to be 13,991 cal./mole, and above the melting point, 10,064 cal./mole. The calculated *heat of fusion* therefore is 3927 cal./mole. From the equation corresponding to the vapor tensions above the melting point, we calculate the Trouton constant to be 22.7 and the normal *boiling point*, 171°. The slightly high value of the Trou-

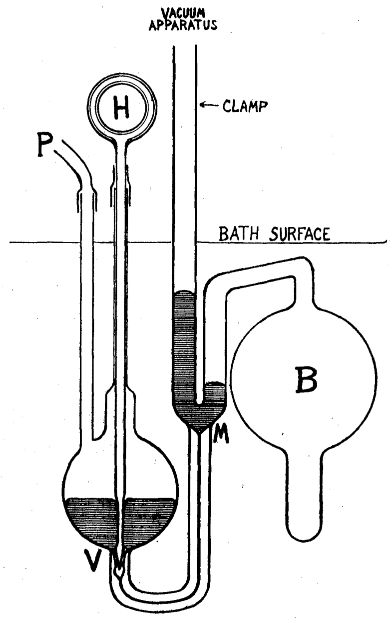

Fig. 2.

ton constant suggests that the true boiling point may be as much as one degree higher.

The sharpness of the melting point, and the character of the vapor tension curves, left no doubt of the uniformity of the material.

The molecular weight was determined by weighing portions of the sample in a small, detachable bulb with stopcock (the grease was not in the least affected), and then measuring the volume by the aid of the special device described above. The data and results of two such determinations are presented in Table VIII. The volume measurements for both of these samples were carried out at temperatures only a little way above the condensation points for the pressures observed; it is therefore reasonable that the results are somewhat higher than the value 72.85, calculated for the formula of borine trimethylammine, $(CH_3)_3NBH_3$.

TABLE VIII

Vol. of bulb, cc.	Temp., °C.	Corr. press.	Sample vol., cc.	Sample wt., mg.	Mol. wt.
118.0	120.0	111.0	11.97	39.6	74.0
118.6	99.5	74.9	8.56	28.6	74.8

This new compound forms hexagonal crystals which may appear in a variety of shapes, from long needles to short lumps having the appearance of broken quartz. Observations indicated that it is very stable, for it was heated at 125° for hours at a time, without the least permanent effect.

The Reaction of Diborane with Trimethylamine.—Diborane is absorbed by trimethylamine (present in 50% excess) rapidly and completely at any temperature at which the latter exerts an appreciable vapor tension. After removal of the excess of trimethylamine, there remains a solid residue having the empirical constitution and properties of borine trimethylammine. It was thought possible that the primary product of the reaction might be an analog of the ammonium salt which is formed by the absorption of diborane by solid ammonia under similar conditions, but an investigation of the behavior of the product toward sodium in liquid ammonia, soon gave an answer to the contrary.[17] The details of an experiment representing these observations are as follows.

A 7.1-cc. sample of diborane was condensed completely upon 20.8 cc. of trimethylamine in the bottom of a plain vertical tube. The tube was then warmed from -196 to $-110°$; the pressure developed by the evaporated diborane diminished practically to zero during five minutes. The excess trimethylamine was then distilled off at $-80°$, and measured as 6.5 cc. The residue hence had the empirical constitution $B_2H_6\cdot 2N(CH_3)_3$, or $BH_3\cdot N(CH_3)_3$, within the probable error.

Ammonia was now distilled into the tube, in quantity sufficient to form 3–4 cc. of solution, and approximately 20 mg. of pure sodium was introduced into the tube, which was kept full of pure hydrogen and at $-196°$ during the process. After the tube was resealed and evacuated, it was warmed to $-75°$; the melting ammonia dissolved the sodium and the solid compound. During five minutes at $-75°$, the solution yielded 0.185 cc. of hydrogen; after half an hour the total hydrogen was only 0.203 cc. It appears reasonable to attribute the hydrogen to impurity, rather than to any appreciable quantity of trimethylammonium ion.

After the solvent ammonia had been removed (by distillation at $-60°$), the residual solid compound was sublimed into the device represented in Fig. 2, and found to exert a vapor tension of 86 mm. at 100°; the melting point was 95°. The volume was measured as 13.2 cc. These results left no doubt that the product of reaction of diborane with trimethylamine is borine trimethylammine. In addition, the molecular weight of a similar sample, which had not been exposed to sodium in liquid ammonia, was measured as 75.6, in good agreement with the values obtained for samples derived from borine carbonyl.

The behavior of trimethylamine toward diborane is thus found to be strikingly different from that of ammonia. At the present time, we see no very clear explanation for the wide contrast between the two reagents.

Acknowledgments.—Credit is due to David M. Ritter for the initial experiment on the reaction of diborane with trimethylamine. We wish also to acknowledge the aid of a grant from the National Research Council, for liquid nitrogen used in this work.

Summary

The new compounds borine carbonyl, BH_3CO, and borine trimethylammine, $(CH_3)_3NBH_3$, have been prepared and characterized. The former decomposes easily, to form diborane and carbon monoxide; the variation in the rate of this decomposition is such as to suggest that free molecules of borine, BH_3, may be involved in the process. Borine trimethylammine, a very stable compound, is formed very easily by the action

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(17) The diammoniate of diborane reacts with sodium in liquid ammonia to produce hydrogen; the experimental details and conclusions will be published in a separate paper. The product of the reaction of diborane with trimethylamine at low temperature does not react at all with sodium in liquid ammonia. The difference cannot be due to a failure of trimethylammonium ion to react with sodium, for a separate experiment showed that trimethylammonium chloride reacts with sodium in liquid ammonia in just the same manner as ammonium chloride does.

of trimethylamine upon either borine carbonyl or diborane. The behavior of ammonia toward diborane and toward borine carbonyl is quite different from that of trimethylamine toward these reagents.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 10, 1937

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

Principal Optical and Physical Properties of the Carbon Tetrachloride Solvate of Rotenone

BY ERNEST L. GOODEN AND CHARLES M. SMITH

For several years chemists and manufacturers working with rotenone have been familiar with the carbon tetrachloride solvate, in which one molecule of rotenone is combined with one molecule of carbon tetrachloride of crystallization ($C_{23}H_{22}O_6 \cdot CCl_4$).[1] Since this solvate is of great practical importance, especially in the analysis of derris and cubé, it was considered necessary to determine its principal optical and physical properties.

The material used for the study was a sample of rotenone that had been recrystallized several times and subjected to microdetermination of carbon and hydrogen to gain assurance of purity.[2] A portion of this analyzed sample was recrystallized from carbon tetrachloride to form the carbon tetrachloride solvate.

Optical Crystallographic Properties

The optical properties investigated were such as are determinable by the use of the petrographic microscope. The solvate crystals were colorless, with a typical elongated, somewhat flattened prismatic shape (Fig. 1). The crystals were found to be biaxial with the following refractive indices (white light): $\alpha = 1.563$, $\beta = 1.612$, $\gamma = 1.631$. The indication of negative optical character obtained by the selenite plate is fairly distinct, and the observed value of β is so much nearer γ than α as to allow no doubt that the character is truly negative. In all cases observed the elongation is negative, the long edges of the crystal lying in the vibration direction for α. Extinction is sensibly parallel at all stages of rotation about the axis of crystal length, which is the vibration direction for α. It is concluded that the crystal belongs in the orthorhombic system.

Density

The density of the crystals was measured with a pycnometer, with water as the displaced liquid. In view of the volatility of the solvate, the accuracy attainable under the conditions of the experiment is considered as extending to two decimal places only. The observed value is 1.40 g. per cc. at 30°. A comparison of the density of the solvate with the densities of rotenone and carbon tetrachloride indicates that practically no volume change accompanies the combination.

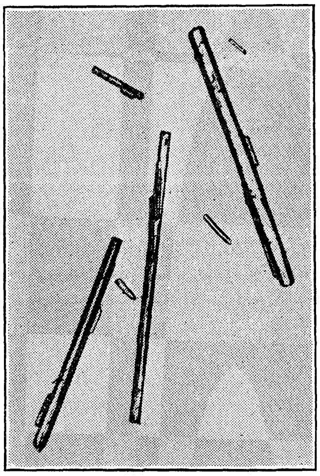

Fig. 1.—Carbon tetrachloride solvate of rotenone (× 175).

Dissociation Pressure

The dissociation pressure was investigated by the static method of vapor pressure measurement.[3] The source of controlled heating for the sample was the vapor above a boiling bath of a pure liquid, acetone, carbon tetrachloride and trichloroethylene being used separately for observations at their respective boiling points.

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[1] H. A. Jones, THIS JOURNAL, **53**, 2738 (1931).

[2] This is the sample referred to by Gooden and Smith, *ibid.*, **57**, 2116 (1935), as having been analyzed by J. R. Spies.

[3] The apparatus used was one constructed by O. A. Nelson, a modification of the apparatus described by Nelson and Senseman, *J. Ind. Eng. Chem.*, **14**, 58 (1922).

The temperature readings were corrected by the established correction curve for the individual thermometer, and the manometer readings were corrected for temperaure of the mercury. With each bath liquid the rise in pressure in the space above the sample was observed repeatedly and the gas was released (for the elimination of air) between successive sets of observations, until a sufficiently precise determination of limiting pressure for given temperature was obtained. Two observed values of limiting pressure were obtained with each of the three baths, giving six points for determination of the vapor pressure curve. When these points were plotted as log pressure (in millimeters of mercury) against reciprocal of absolute temperature, they were found to lie almost exactly in a straight line. The best fitting straight line was calculated,[4] and is expressed by the equation

$$\log P = 9.308 - (2313/T)$$

where P is the pressure in millimeters of mercury and T is the temperature on the absolute (Kelvin) scale. The six points and the calculated line are shown in Fig. 2.

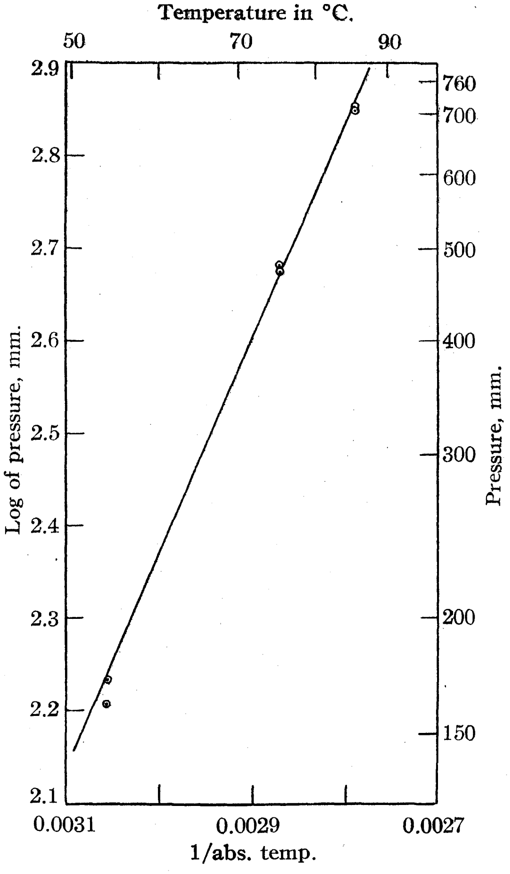

Fig. 2.—Dissociation pressure of the carbon tetrachloride solvate of rotenone (pressure of CCl_4 vapor over $C_{23}H_{22}O_6 + C_{23}H_{22}O_6 \cdot CCl_4$).

This equation leads to a value of 87° for what may be termed the "decomposition temperature" of the solvate, in the sense of the temperature at which the carbon tetrachloride vapor reaches normal atmospheric pressure. The heat of dissociation–vaporization as calculated on the basis of the same equation is 69 cal. per gram of carbon tetrachloride, which is approximately 23 cal. per gram in excess of the heat of vaporization of carbon tetrachloride at the same temperature. These results indicate that the solvate is so unstable as to require careful sealing for storage.

Additional Comparisons and Checks

It is interesting and worth while to compare the optical properties of the carbon tetrachloride solvate of rotenone with those of rotenone itself in the common (m. p. 163°) form. The indices β and γ of the solvate nearly coincide, respectively, with α and β of rotenone (α = 1.616, β = 1.635, γ = 1.662); the maximum birefringence, however, is one and one-half times as great in the solvate as in rotenone. The specific refraction is conspicuously lower in the solvate, as would be expected from the fact that the specific refraction of carbon tetrachloride is approximately 36% lower than that of rotenone. The calculated molecular refraction cannot be arrived at precisely because of the complex structure of rotenone. The various calculated values for the molecular refraction of the solvate are all very close to 129 (cubic centimeters per mole, according to Lorentz–Lorenz formula), if no allowance is made for a linkage refraction for the combination of the rotenone molecule with the carbon tetrachloride molecule. The observed molecular refraction is 134, this value being nearly equal to the sum of the observed molecular refraction (107) for rotenone and the observed value (26.45) for carbon tetrachloride.

Summary

The carbon tetrachloride solvate of rotenone, $C_{23}H_{22}O_6 \cdot CCl_4$, has been studied with respect to refractive indices, density and dissociation pressure.

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[4] One of the six points, the lowest, showed an appreciable departure from a straight line, and was therefore disregarded; the line was calculated from the other five points by the method of least squares.

The principal results of the optical determinations are: $\alpha = 1.563$; $\beta = 1.612$; $\gamma = 1.631$; optical character, negative; elongation, commonly negative; system, orthorhombic.

The density at 30° is 1.40 g. per cc.

The dissociation pressure in the range 60 to 90° is expressed by the equation $\log P_{\text{mm.}} = 9.308 - (2313/T_K)$. The "decomposition temperature" is consequently 87°, and the heat of dissociation–vaporization 69 calories per gram of carbon tetrachloride.

WASHINGTON, D. C.

RECEIVED FEBRUARY 17, 1937

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 584, AND THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Crystal Structure of Selenium Dioxide

BY JAMES D. MCCULLOUGH

Quoting measurements made by C. F. Rammelsburg, Groth[1] describes selenium dioxide as monoclinic prisms with $a:b:c = 1.292:1:1.067$. He states that the measurements were only approximate, however, due to the extreme hygroscopic nature of the crystals, which made rapid work necessary. All crystals examined in the present work were found to be tetragonal needles with the axial ratio $a:c = 1:0.6047$.

Method of Preparation.—Pure selenium dioxide was dried at approximately 200° in a stream of oxygen which had been passed first through a tube containing phosphorus pentoxide. After drying for several hours, the Pyrex tube containing the selenium dioxide was sealed off at both ends and the substance was sublimed very slowly in an electric furnace. The atmosphere of oxygen prevented the decomposition which sometimes accompanies sublimation of the oxide in the open. The tube was opened inside a moisture-free box and selected crystals were mounted in moisture-proofed gelatine capsules. Except when being photographed they were kept in a desiccator. These precautions were found necessary in order to preserve the crystal faces and prevent lines due to selenious acid appearing on the photographs.

The crystals were transparent, colorless needles about 2–10 mm. long and 0.2–0.5 mm. thick with (100), (110) and (111) principally developed.

The Unit Cell and Space-Group

Laue photographs prepared with the incident beam perpendicular to a (100) face showed a vertical as well as a horizontal plane of symmetry as did the photographs normal to a (110) face. The tetragonal nature of the crystals was established by noting that a rotation of 90° about the needle axis gave a Laue photograph indistinguishable from the original one. Further evidence was furnished by the fact that the photographs prepared with the x-ray beam parallel to the needle axis showed a fourfold axis and four planes of symmetry at 45° intervals. The Laue symmetry thus indicated is that of D_{4h}.

A complete set of 15° oscillation photographs was prepared using unfiltered copper radiation with a 5-cm. camera. The oscillation was about the c-axis. One 30° oscillation photograph was prepared using [110] as an axis but was not very satisfactory for intensity considerations due to the shape of the crystal. Attempts to cleave the crystals across the needle or c-axis were unsuccessful and resulted in shattering.

From these photographs the unit edges $a_0 = 8.353 \pm 0.005$ Å. and $c_0 = 5.051 \pm 0.010$ Å. were calculated. Using these dimensions, values of $n\lambda$ were calculated for a completely indexed Laue photograph in which the x-ray beam made an angle of about 2° with the a-axis. The smallest value thus found was $n\lambda = 0.245$ Å. from (810), the short wave length limit being 0.24 Å.

The oscillation photographs and the first order reflections on the indexed Laue photograph showed all varieties of (hkl) and ($hk0$) reflections. The lattice is accordingly simple. Reflections of the type (hhl) were not observed for l odd although many such planes were in position to reflect, especially on the oscillation photograph about [110]. Further, ($h0l$) was not observed for h odd. These conditions indicate D_{4h}^{13} – $P4/mbc$ or C_{4v}^{8} – $C4cb$ as probable space groups. Attempts to detect a pyroelectric effect failed, but this may have been due to the hygroscopic

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[1] P. Groth, "Chemische Kristallographie," Vol. I, 1906, p. 93.

nature of the crystals. Hence, no further choice of space group can be made at this point.

The Atomic Arrangement

The density of selenium dioxide is given by Clausnizer[2] as 3.95. This value requires 7.59 molecules in the unit. On the assumption of 8 molecules of selenium dioxide in the unit cell, the calculated density is 4.17 g./cc. We have, therefore, to place 8Se and 16O within the cell. Since the selenium atoms will do most of the scattering, to a first approximation we may overlook the oxygen. By means of simple considerations, all positions[3] were excluded to selenium except 8*g* and 8*h* of D_{4h}^{13} and 8*c* of C_{4v}^{8}. At this point some difficulty was encountered so it was considered advisable to resort to the two-dimensional Patterson method[4] in view of the excellent (*hk*0) data available.

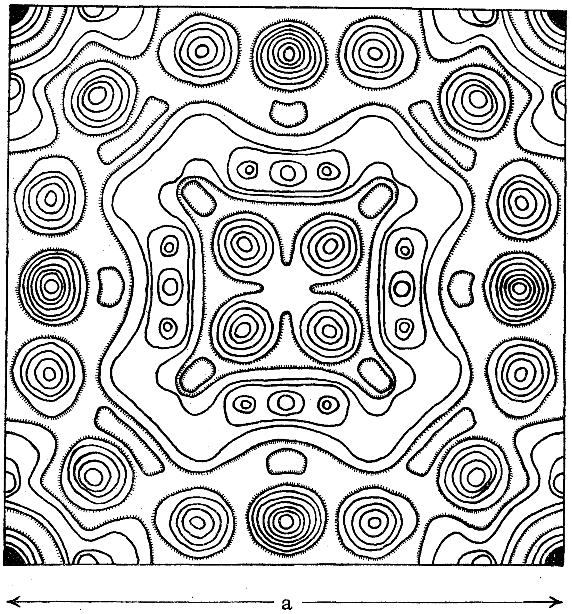

Fig. 1.—Plot of the function $p(x, y)$. Maxima represent the projection of interatomic distance vectors on the plane (001).

The two dimensional Fourier series

$$p(x, y) = \text{constant}\ \Sigma_h \Sigma_k\ |F_{hk0}|^2 \cos 2\pi(hx + ky) \quad (1)$$

will have maxima corresponding to the projection of the interatomic distance vectors on the (001) face of the unit cell. In evaluating this series the values of $|F_{hk0}|^2$ shown in Table I were used. These values were obtained from the visually estimated intensities by use of the equation

$$|F_{hk0}|^2 = \frac{2I_{hk0} \sin 2\Theta}{1 + \cos^2 2\Theta} \quad (2)$$

In estimating the intensities a graduated comparison film of timed exposures was used. The function was evaluated at intervals of *x* and *y* corresponding to $1/48\ a_0$. The result is plotted in Fig. 1. The principal maxima are without doubt due to selenium–selenium interactions and correspond to the positions 8*h* of D_{4h}^{13} or 8*c*

TABLE I

EQUATORIAL REFLECTIONS FOR SELENIUM DIOXIDE

hkl	Intensity of reflection Obsd.	Intensity of reflection Calcd.	Obsd. $\lvert F_{hkl} \rvert^2$	Obsd. F_{hkl}
110	47	66	13	3.6
200	350	410	135	−11.6
210	150	216	65	− 8.1
220	0	0	0	0
310	50	67	34	− 5.8
320	45	48	35	− 5.9
330	36	63	35	5.9
400	100	106	91	− 9.6
410	0	0.4	0	0
420	49	65	51	7.2
430	19	14	23	− 4.8
440	35	22	51	− 7.2
510	40	31	50	7.1
520	28	20	37	6.1
530	13	7	19	− 4.4
540	25	21	45	− 6.7
550	35	44	68	− 8.3
600	8	13	12	3.5
610	150	152	245	15.7
620	1	0.8	1.5	− 1.2
630	0	.1	0	0
640	2.5	.2	5	− 2.2
650	33	22	66	− 8.1
660	0	0.2	0	0
710	11	9.0	21	− 4.6
720	1.5	5.0	3.0	1.7
730	9	6.4	17	4.1
740	8	7.3	15	− 3.9
750	45	42	82	9.1
760	1.0	2.1	1.5	− 1.2
770	100	126	103	−10.2
800	3.0	2.4	6.0	2.5
810	35	38	70	− 8.4
820	18	11	34	− 5.8
830	5	3.3	9	− 3.0
840	20	20	34	5.8
850	20	21	26	5.1
860	0	0	0	0
910	7	4.7	11.5	3.4
920	23	28	34	− 5.8
930	22	21	29	− 5.4
940	33	33	36	6.0
10·0·0	2	2	2	1.4
10·1·0	14	17	14	− 3.7
10·2·0	10	5	8	2.8

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(2) Clausnizer, *Ann.*, **196**, 272 (1879).

(3) R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Publication of the Carnegie Institute of Washington, 1922.

(4) A. L. Patterson, *Z. Krist.*, **90**, 517 (1935).

of C_{4v}^{8} with parameters $x = 0.13$ and $y = 0.21$. Maxima due to selenium–oxygen interactions with a separation of 1.25 Å. on the projection occur along the edges of the plot. Because of the symmetry properties of the space-groups under consideration, each crystallographically different set of atoms must produce one or more maxima along the diagonal of the plot. In order to increase the probability of finding the oxygen atoms and in order to get better values of the selenium parameters, the diagonal was evaluated in units corresponding to 1/240 a_0. The result is shown in Fig. 2. The larger selenium–selenium peaks occur at $x_1 = 0.161$ and $x_2 = 0.427$. Since

$$\begin{aligned} x_{\mathrm{Se}} + y_{\mathrm{Se}} &= \tfrac{1}{2} - x_1, \text{ and} \\ x_{\mathrm{Se}} - y_{\mathrm{Se}} &= \tfrac{1}{2} - x_2 \end{aligned} \tag{3}$$

the selenium parameters are $x = 0.133$ and $y = 0.206$. The smaller maximum at $x = 0.284$ was considered to be due to 8O in the positions $8g$ of D_{4h}^{13} or the equivalent in C_{4v}^{8}. The corresponding parameter x_O is obtained by the relationship $2x_O = 1 - x$, from which $x_O = 0.358$. This assumption was considered reasonable since it also accounts for the previously mentioned selenium–oxygen separation both in direction and in magnitude.

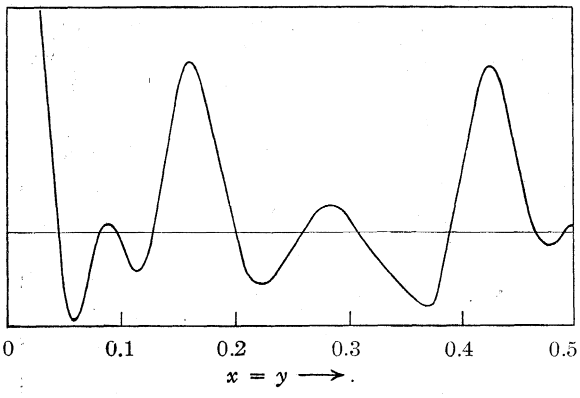

Fig. 2.—Half-diagonal of the function p (x, y).

This still leaves 8O unaccounted for and maxima due to them are either hidden by the larger interactions already mentioned or they fail to appear due to inaccuracies in the intensity data or because of an insufficient number of terms in the summation. In order to locate these oxygen atoms and to further verify the results already obtained, a two-dimensional Fourier synthesis was made using the series

$$\rho\ (x, y) = \text{constant}\ \Sigma_h\Sigma_k\ F_{hk0} \cos 2\pi(hx + ky) \tag{4}$$

The maxima in this case will correspond to the projection of the atomic positions on the plane (001). In carrying out this summation, intervals corresponding to 1/96 a_0 were employed in x and y. The algebraic sign of F_{hk0} was determined in each case from the selenium parameters already given, on the assumption that all the scattering was due to selenium. These signs were later checked and only one minor change was needed. The F_{hk0} values are shown in Table I.

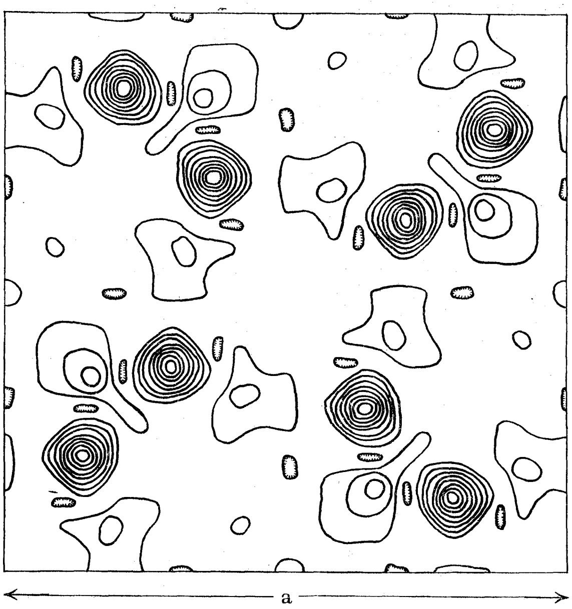

Fig. 3.—Plot of the function ρ (x, y) for selenium dioxide. Projection of scattering matter on (001).

The result of the Fourier summation is shown in Fig. 3. It is seen that the previous findings are confirmed and the remaining oxygens located. The whole projection can be interpreted in terms of either D_{4h}^{13} or C_{4v}^{8} with similar x and y parameters. The final choice was made by means of the layer line intensities which are accounted for nicely by the structure based on D_{4h}^{13} having the following atomic positions

8Se in 8*h*

$x, y, 0;\ \bar{x}, \bar{y}, 0;\ \tfrac{1}{2} + x, \tfrac{1}{2} - y, 0;\ \tfrac{1}{2} - x, \tfrac{1}{2} + y, 0;$
$\bar{y}, x, \tfrac{1}{2};\ y, \bar{x}, \tfrac{1}{2};\ \tfrac{1}{2} + y, \tfrac{1}{2} + x, \tfrac{1}{2};\ \tfrac{1}{2} - y, \tfrac{1}{2} - x, \tfrac{1}{2}.$

$8O_{I}$ in 8*g*

$x, \tfrac{1}{2} + x, \tfrac{1}{4};\ \bar{x}, \tfrac{1}{2} - x, \tfrac{1}{4};\ \tfrac{1}{2} + x, \bar{x}, \tfrac{1}{4};\ \tfrac{1}{2} - x, x, \tfrac{1}{4};$
and corresponding positions with $z = \tfrac{3}{4}$.

$8O_{II}$ in 8*h*.

with parameter values from the Fourier plot
$x_{\mathrm{Se}} = 0.133 \pm 0.001;\ y_{\mathrm{Se}} = 0.207 \pm 0.002$
$x_{O_I} = .358 \pm .005$
$x_{O_{II}} = .425 \pm .010;\ y_{O_{II}} = .320 \pm .010$

These parameter values are seen to be in good agreement with those obtained by the Patterson method.

Intensities were calculated for the equator and first two layer lines by means of the equation

$$I_{hkl} = \text{constant}\ [\Sigma_j f_j\, e^{2\pi i(hx_j + ky_j + lz_j)}]^2\ \frac{1 + \cos^2 2\Theta}{2 \sin 2\Theta} \qquad (5)$$

The Pauling–Sherman f-values[5] were used for f_j and the atomic coördinates x_j, y_j, z_j are the parameter values given above. No temperature factor was introduced. The observed and calculated equatorial intensities are given in Table I, while those for the layer lines occur in Table II. The agreement is believed sufficiently good to establish the structure as correct.

TABLE II

LAYER-LINE REFLECTIONS FOR SELENIUM DIOXIDE

	First layer line Intensity			Second layer line Intensity	
hkl	Obsd.	Calcd.	*hkl*	Obsd.	Calcd.
201	205	240	312	88	96
211	190	263	322	80	73
311	41	36	332	115	116
321	31	26	402	2.4	4.8
401	195	213	412	7.3	7.6
411	77	74	422	37	30.4
421	62	70	432	33	15.9
431	2.6	2.1	442	64	51.5
511	42	56	512	14	14.4
521	1.5	3.0	522	57	55
531	71	114	532	3.3	2.2
541	35	30	542	40	28
601	1	0.04	552	40	33
611	3	2.9	602	0	1.3
621	3.5	2.2	612	55	71
631	51	47	622	0	0.1
641	5	2.1	632	2.4	1.6
651	40	34	642	4	1.7
711	21	21	652	8	6.1
721	0	0	662	1.6	1.7
731	46	46	712	1.6	1.0
741	1.4	0.8	722	3.1	4.8
751	2.6	2.5	732	0	0
761	10	4.2	742	8	7.3
801	41	55	802	0	0
811	1	1.0	812	33	21
821	14	11	822	16	15
831	24	17	832	0	0.9
841	0	0.2	842	57	42
851	31	17			
861	0	0.02			
911	2.6	2.5			
921	0	0.2			
931	10	4.0			
941	9	4.4			
951	10	12			
10·0·1	57	79			
10·1·1	62	69			

Discussion of the Structure

The structure found for selenium dioxide is shown in Figs. 4 and 5. It is to be noted that the oxygen atoms are of two kinds, both crystallographically and chemically. Accepting small interatomic distances as showing bonds, we see that the oxygen atoms of the first type are bonded to two selenium atoms while those of the second type are bonded to only one. Since each selenium atom is bonded to two oxygen atoms of type one and to one of type two, the result is a series of flat chains parallel to the c-axis of the crystal. The selenium atoms in a given chain all lie in a plane which is parallel to (110). The oxygen atoms of the second type lie in another plane also parallel to (110), while the remaining oxygen atoms are in between, somewhat closer to the plane of the oxygen atoms of type two than to the selenium plane. This causes a difference in charge on either side of the chain, the selenium surface being positive and the oxygen surface negative. The chains are probably held together by the electrostatic attraction of the oxygen atoms in one chain for the selenium atoms in a neighboring chain, which effect would be enhanced by the staggering of atoms which occurs. The chain structure ties in with observance of a fair prismatic cleavage parallel to (100) and (110), and the lack of cleavage parallel to (001).

The observed interatomic distances are 1.78 ± 0.03 Å. for Se–$\mathrm{O_I}$ and 1.73 ± 0.08 Å. for Se–$\mathrm{O_{II}}$. The sum of the normal single bond radii is 1.83 Å., taking 1.17 Å. for selenium and 0.66 Å. for oxygen.[6] The nearest approach of two oxygen atoms is 2.53 Å. for $\mathrm{O_I}$–$\mathrm{O_I}$ and 2.67 Å. for $\mathrm{O_I}$–$\mathrm{O_{II}}$, while the distance between selenium atoms in the same chain is 3.16 Å. The observed bond angles are 98 ± 2° for $\mathrm{O_I}$–Se–$\mathrm{O_{II}}$, 90° ± 30′ for $\mathrm{O_I}$–Se–$\mathrm{O_I}$ and 125° ± 30′ for Se–$\mathrm{O_I}$–Se.

The observed Se–$\mathrm{O_I}$ distance is in fairly good agreement with the value expected for a single covalent bond, but one would expect the oxygen atoms of the second type to be doubly bonded to selenium with a separation of approximately 1.64 Å. When $\mathrm{O_{II}}$ parameters are chosen to satisfy this double bond distance, the calculated intensities are not quite as satisfactory in general, although the changes are not great. The $\mathrm{O_{II}}$ parameters given were taken as the

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(5) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(6) L. Pauling and M. L. Huggins, *ibid.*, **87**, 205 (1934).

highest points due to these atoms on the Fourier plot. Actually the closeness of the large selenium maxima may be of influence here and perhaps one should take the highest point above the sloping selenium maximum in the background. Efforts to get a good estimate of this influence were without success due to the ever-present fluctuations introduced when one evaluates an infinite series of this kind by means of a finite number of terms. Further, the estimated intensities used in the summation may have been somewhat in error.

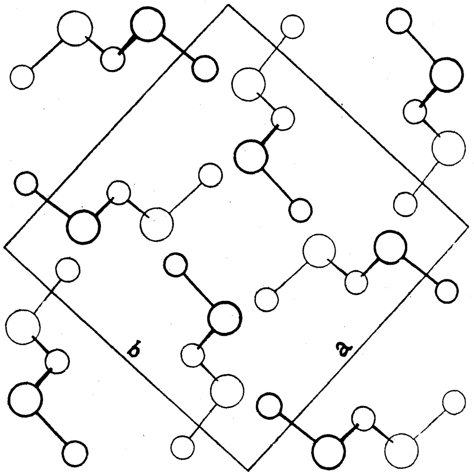
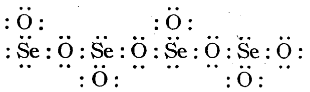


Fig. 4.—Projection of the selenium dioxide structure on the (001) face of the unit. The chains are seen end-on. Large circles indicate selenium atoms, while small circles represent oxygen.

It is interesting to note that selenium dioxide molecules as such do not exist in the solid. However, only one single covalent bond must be broken per selenium dioxide molecule produced in the vapor state. This may account for the relatively high vapor pressure of the solid as shown by its ease of sublimation. The probable electron configuration is



$$\begin{array}{cccccccc} :\overset{\cdot\cdot}{O}: & & & & :\overset{\cdot\cdot}{O}: & & & \\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Se}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{Se}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{Se}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{Se}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \\ & & :\underset{\cdot\cdot}{O}: & & & & :\underset{\cdot\cdot}{O}: & \end{array}$$

with an unshared pair of electrons occupying the fourth tetrahedral position of selenium. The shortening of the selenium–oxygen bonds, especially that for oxygen of the second type, may be attributed to partial double bond character brought about by an unshared pair from oxygen swinging into the bonding position for a fraction of the time. This gives selenium more than eight electrons in its valence shell, and it is probably the resistance to this breaking of the octet rule which prevents permanent double bonds from selenium to oxygen. Assuming a relationship between interatomic distance and percentage of double bond character similar to that for the carbon–carbon bond,[7] it is estimated that the Se–O_I bonds have 10–15% and the Se–O_{II} bonds 20–25% of double bond character.

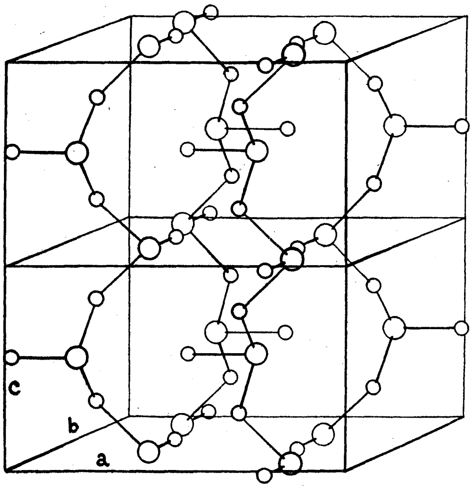


Fig. 5.—Atomic arrangement of selenium dioxide showing two unit cells. Large circles represent selenium atoms and small circles oxygen.

Another feature of the structure worth-while mentioning is that each selenium atom is surrounded by an irregular octahedron of six oxygen atoms. This octahedron consists of two O_I at a distance of 1.78 Å., one O_{II} at 1.73 Å., one O_{II} at 2.63 Å. and two O_{II} at 3.00 Å. The first three atoms belong to the same chain as the selenium while the remaining three belong to neighboring chains.

The author wishes to express thanks to Professor Linus Pauling for his helpful suggestions during the structure determination and to Dr. James H. Sturdivant for much valuable advice and assistance in preparing the X-ray photographs.

Summary

By means of an X-ray investigation, sublimed selenium dioxide has been shown to crystallize in the tetragonal system with unit edges a_0 = 8.353 ± 0.005 Å. and c_0 = 5.051 ± 0.010 Å. The unit of structure contains eight selenium

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[7] L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

and sixteen oxygen atoms in the following positions of the space group D_{4h}^{13}:

8Se in 8*h* with $x = 0.133$ and $y = 0.207$
$8O_I$ in 8*g* with $x = 0.358$
and $8O_{II}$ in 8*h* $= 0.425$ and $y = 0.320$

The structure consists of chains of alternating selenium and oxygen atoms along the *c*-axis, with oxygen of a second kind bonded to each selenium atom. The observed separations are 1.78 ± 0.03 Å. for Se–O_I and 1.73 ± 0.08 Å. for Se–O_{II} with bond angles of 98 ± 2° for O_I–Se–O_{II}, 90° ± 30′ for O_I–Se–O_I and 125° ± 30′ for Se–O_I–Se.

LOS ANGELES, CALIF. RECEIVED FEBRUARY 17, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Validity of Raoult's Law for Paraffin Molecules of Very Different Length

BY JOEL H. HILDEBRAND

An interesting and fundamental question was raised during the recent symposium of the Faraday Society by Guggenheim,[1] who pointed out that the ordinarily accepted validity of Raoult's law for solutions whose components possess equal molecular fields has no sure foundation in statistical mechanics except for cases which correspond to the simple model in which molecules are spherical and "sufficiently alike so that each molecule of either species is directly surrounded by the same number of other molecules. Up to the present no one has succeeded in applying statistical mechanics to a more general model." In the discussion which followed the presentation of this paper the writer called attention to various pieces of experimental evidence indicating that the effect, if it exists, is probably a small one, as indeed the formulation by Guggenheim indicated; nevertheless, the modern treatment of solutions on the basis of their deviations from Raoult's law makes the theoretical support of this law a matter of considerable importance. The purpose of this paper is to follow up a suggestion, made during the discussion, of a model which does lend itself to statistical treatment and which, fortunately, corresponds to the actual solutions most appropriate for experimental tests of the matter: those of normal paraffins of different molecular weight. These furnish, moreover, the cases likely to be of greatest practical importance.

Our model will consist of two molecular species of identical cross section but different lengths, close-packed with their axes parallel. The longer paraffin chains are evidently parallel in the solid state and are probably not much disturbed from a similar "cybotactic" grouping in the liquid state.[2] Furthermore, the field strength of such molecules is surely the same function of the distance from the axis, *e. g.*, to separate a decane molecule from another decane molecule, parallel and in "contact," requires the same energy as to separate it from two pentane molecules, except for a slight effect due to the ends, which becomes proportionally still less for longer chains. The intermolecular distances are not strictly the same for the longer and the shorter molecules at the same temperature, for the latter possess a greater amplitude of motion for the same thermal energy. This difference, however, can be minimized by using longer molecules or lower temperatures. This point will be evident from the lower curve in Fig. 1, where the heat of vaporization per gram, $\Delta H/m$, is plotted against the temperature. The values are all evidently asymptotic to a common line as temperature is lowered. The divergence appears to be almost entirely due to more rapid expansion for the lighter species with rising temperature, as shown by the upper curve in Fig. 1, in which $V\Delta E/m^2$ is plotted against temperature, where V is the molal volume, ΔE, the molal energy of vaporization and *m*, the molecular weight. This is equivalent to the product of the volume and heat of vaporization per gram. The departures from a common line appear to be within the experimental errors.

Raoult's law is most often written in the form $p_1 = p_1^0 N_1$, where p_1 is the partial vapor pressure of one component, p_1^0 its vapor pressure in the pure liquid state and N_1 its mole fraction. For the present purpose we shall substitute fugacity, *f*, for vapor pressure. Raoult's law is then

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[1] E. A. Guggenheim, *Trans. Faraday Soc.*, **33**, 151 (1937).

[2] G. W. Stewart, *Phys. Rev.*, **31**, 174 (1928); A. Müller, *Trans. Faraday Soc.*, **29**, 990 (1933); R. Rigamonti, *Gazz. chim. ital.*, **66**, 174 (1936).

$f_1 = f_1^0\mathrm{N}_1$. Raoult's law follows from simple statistical considerations in the case of two molecular species of identical size and field, but not for species of unequal field and not obviously for those of unequal size. It might seem, offhand, that the fugacity of a hydrocarbon molecule should be proportional to its volume concentration, *i. e.*, $f = kn/\mathrm{V}$, since it is under the same constraints regardless of whether its neighbors are a certain number of, say, decane molecules or half as many eicosane molecules, which would correspond to a very different mole fraction. I have already shown,[3] however, by the aid of the Gibbs–Duhem equation, that the volume concentration can be proportional to fugacity only in the special case that the molal volumes of the components are identical, in which case the above expression reduces to Raoult's law with fugacity proportional throughout to the mole fraction. This does not, of course, prove that the fugacity may not be proportional to some other function of the composition of the solution.

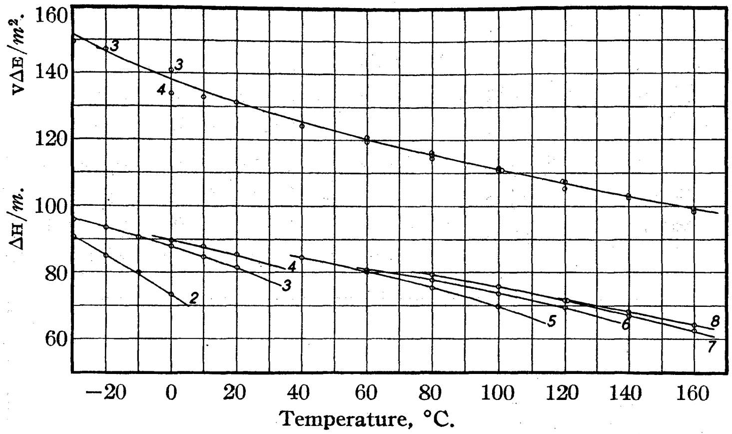

Fig. 1.—Effect of temperature and length of chain for paraffins upon the heat of vaporization per gram and upon the product of this by the specific volume of the liquid.

We may write Raoult's law in the form, $\bar{\mathrm{F}}_1 - \mathrm{F}_1^0 = RT \ln \mathrm{N}$, where $\bar{\mathrm{F}}_1$ is the partial molal free energy and F_1^0 the molal free energy in the pure liquid state. We will split up the free energy according to the general thermodynamic relation, $\mathrm{F} = \mathrm{E} + p\mathrm{V} - T\mathrm{S}$, giving

$$\bar{\mathrm{F}}_1 - \mathrm{F}_1^0 = RT \ln \mathrm{N}_1 = \bar{\mathrm{E}}_1 - \mathrm{E}_1^0 + p(\bar{\mathrm{V}}_1 - \mathrm{V}_1^0) - T(\bar{\mathrm{S}}_1 - \mathrm{S}_1^0)$$

Since we are restricting the case to that in which there is no total energy change on transferring the component from the pure liquid to the solution, we set $\bar{\mathrm{E}}_1 - \mathrm{E}_1^0 = 0$. The next term on the right-hand side is at best small. For example, if we set $\bar{\mathrm{V}}_1 - \bar{\mathrm{V}}_1 = 3$ cc., when $\mathrm{N}_1 = 0$, the order of magnitude seldom exceeded, the term $p(\bar{\mathrm{V}}_1 - \mathrm{V}_1)$ has a maximum value of about 0.07 cal., a quite negligible quantity. Our problem is then to show that, for our model, $-R \ln \mathrm{N}_1 = \bar{\mathrm{S}}_1 - \mathrm{S}_1^0$.

If we follow the analysis of Stern,[4] for the entropy of a solid solution, we can regard the entropy of a lattice as made up, first, of a term due to the difference in specific heat of the molecules in the solution and in the pure substance, and, second, of a term depending upon the number of configurations which the lattice might assume. In the ordinary lattice the number of positions which molecules can occupy is regarded as fixed, and the different configurations are reckoned from the number of different possible arrangements. If the numbers of molecules of the respective species are N_1 and N_2, the total number of lattice positions is $N_1 + N_2$ and the total number of arrangements is $(N_1 + N_2)!$. However, all molecules of one species are alike, hence $N_1!$ are alike and $N_2!$ are alike. The number of different arrangements is then $(N_1 + N_2)!/N_1!N_2!$. In the pure crystal there is only one ($=N_1!/N_1!$) arrangement. The entropy of the mixed crystal is then

$$k \ln \frac{(N_1 + N_2)!}{N_1!N_2!} - k \ln \frac{N_1!}{N_1!} - k \ln \frac{N_2!}{N_2!} = \\ k \ln (N_1 + N_2)! - k \ln N_1! - k \ln N_2!$$

Applying Stirling's formula gives

$$k(N_1 + N_2) \ln (N_1 + N_2) - kN_1 \ln N_1 - kN_2 \ln N_2$$

Differentiating with respect to N_1 at constant N_2 gives $k \ln (N_1 + N_2) - k \ln N_1$. Since the numbers of moles of the components are, respectively, $n_1 = \mathrm{N}_1/N$ and $n_2 = \mathrm{N}_2/N$ where N is Avogadro's number, we get for the transfer of a mole of component one from the pure state to the solution,

$$\bar{\mathrm{S}}_1 - \mathrm{S}_1^0 = -R \ln \frac{n_1}{n_1 + n_2} = -R \ln \mathrm{N}_1$$

In our model of a solution of paraffins, the specific heat term must be practically negligible, hence the entropy must depend mainly upon the possible configurations. It has been customary to calculate the number of configurations as above, with reference to a definite lattice

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(3) J. H. Hildebrand, *Chem. Rev.*, **18**, 315 (1936).

(4) O. Stern, *Ann. Physik*, [4] **49**, 823 (1916); **51**, 237 (1916); *cf.* also, K. F. Herzfeld, *Z. Physik*, **16**, 84 (1923).

of points representing the mean positions of the atoms. This has made it necessary to limit consideration to species so nearly alike in size and shape that a given point-lattice can serve to describe the structure. In the case of paraffins, this would require that the length of the longer chain must be an integral multiple of that of the shorter. I wish to suggest that the lattice of points is, after all, artificial, like a given set of coördinate axes, and that it should be possible to determine the number of configurations in a more general way, applicable, at least, to linear molecules of any relative lengths. I propose, therefore, that the number of configurations be determined for our model by the number of possible interchanges, sliding the intervening molecules along in the direction of their axes sufficiently to furnish the proper space for each. This is most easily seen if we arrange long and short molecules linearly, when it is evident that the number of arrangements is the same as it would be if the molecules were of equal length. We will conclude, therefore, that the above equation holds for our model as truly as for a solution whose molecules are of equal size and field strength.[5]

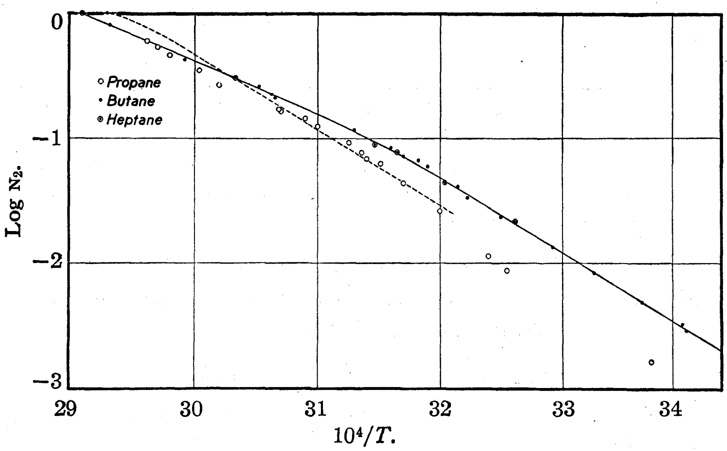

Fig. 2.—Solubility of dicetyl.

The experimental evidence at hand in confirmation of the validity of Raoult's law for solutions of straight paraffins of unequal length is at present rather fragmentary. Indeed, no extremely good agreement is to be looked for, since solutions of paraffins of nearly the same size often show departures from ideal behavior of several per cent., due either to experimental errors or to departures of the vapors from the ideal gas laws. The system investigated from among the lighter paraffins showing the most extreme variation in size is butane–heptane[6] and this obeys Raoult's law very well. Ethane dissolves in heptane almost exactly to the extent demanded by Raoult's law, according to the measurements of McDaniel;[7] however, he reports that its solubility in hexane is much less, which imposes a strain upon one's credulity. The figures for solubility at 20°, calculated to mole per cent., are as follows: ideal, 2.68; in heptane, 2.79; in hexane, 1.84.

Recently Seyer and Fordyce[8] have published solubilities of dicetyl (dotriacontane) in pentane and in heptane. I have had on hand for some time measurements, obtained by Dr. A. Wachter under my direction, of the solubility of this substance in various solvents, including one paraffin, heptane. They were not published because the solubilities in some of the solvents appeared to be larger than the ideal solubility, calculated from the melting point and the heat of fusion. This state of affairs is not known to occur except as the result of solvation, which appeared out of the question in these solutions. The data were therefore withheld pending further confirmation, either experimental or theoretical. Our figures for heptane are here given in Table I and plotted in Fig. 2 in the form of the logarithm of the mole fraction of dicetyl against $1/T$. The results of Seyer and co-workers for propane and butane are shown on the same plot.

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[5] The above analysis was submitted to Professor O. Stern, whose reply is important enough to be here quoted, with his permission.

"This is certainly a very amusing problem. I am convinced you are absolutely right with respect to your result as well as with the method of calculating.

"At first, I was somewhat puzzled because I could not see how to derive your results by the van der Waals theory, but after some thinking I found the solution. Perhaps you will be interested to learn of my troubles and the solution. It is like this:

"Imagine we have in the one-dimensional case a liquid consisting of two long molecules in equilibrium with the vapor phase. Now, if we break up one of the long molecules into three small ones, we would at first sight, expect the vapor pressure of the long molecules to be one-half of the previous value; because the value of van der Waals b should not be changed by this process. But according to your theory, the vapor pressure should be one-fourth. Now the solution is this: The value of the volume, v, changes. If we call the van der Waals $(v - b)$ the 'effective volume,' then this 'effective volume' is proportional to the number of molecules in the liquid; so that the 'effective volume' for the large molecule is four times as large and the vapor pressure four times as small."

[6] G. Calingaert and L. B. Hitchcock, THIS JOURNAL, **49**, 750 (1927); *cf.* H. A. Beatty and G. Calingaert, *Ind. Eng. Chem.*, **26**, 504 (1934); S. Young and E. C. Fortney, *J. Chem. Soc.*, **83**, 45 (1903).

[7] McDaniel, *J. Phys. Chem.*, **15**, 587 (1911).

[8] W. F. Seyer and R. Fordyce, THIS JOURNAL, **58**, 2029 (1936).

TABLE I

SOLUBILITY OF DICETYL IN *n*-HEPTANE

t, °C.	G. per 100 g.	Mole, %
28.4	4.11	0.905
29.8	4.98	1.095
34.2	8.68	1.89
35.0	10.23	2.22
39.0	20.8	4.42
43.0	36.0	7.41
44.6	44.2	8.95
56.6	198.6	30.6

The nature of the difficulty has recently come to light. It is due to a transition in the solid below the melting point which alters the form of the curve for the ideal solubility. Garner[9] and co-workers have determined the heats of transition and fusion for the normal paraffin hydrocarbons containing 22, 26, 30, 34 and 35 carbon atoms. By interpolating their results we may obtain data for dicetyl, for the molal heat of fusion of the α-form, the heat of transition α to β and the molal heat capacities of the liquid α and β forms. We may then calculate the ideal solubility curve of the α-form from its melting point down to the transition point and the ideal solubility of the β-form from there down. We cannot at present place too much confidence in the result of this calculation, however, on account of some uncertainty regarding the data. The fusion temperature of dicetyl interpolated from the data of Garner and co-workers is 68.4° while the transition temperature is 63.5°. The dicetyl used by Wachter, however, melted at 70.2°. Delcourt,[10] in Timmermans' Laboratory, has found 70° for the melting point, and Deffet[11] reports a melting point of 70.0° and a transition point of 64.3°. The material used by Seyer and Fordyce melted at 69.9°. They also give 55° for the transition temperature. It is possible that the transition between α and β is not a sharp change. Their curve for refractive index against temperature shows no sudden jump at 55° but rather a gradual rise between 55 and 70°. The data of Garner and co-workers for tetratriacontane show a rather rapid increase in the heat content of the β-form as the transition is approached and a somewhat rounded, continuous rather than sharply discontinuous change through the α to the liquid. This behavior is by no means uncommon.[12] It can be handled readily by plotting the heat content per mole of substance from some common lower temperature against $1/T$ and integrating graphically down from the melting point between this curve and the extrapolated heat content curve for the liquid, since $-\log \text{N} = (1/4.575) \int \Delta\text{H}d(1/T)$. The dotted line in Fig. 2 has been obtained in this way using data by Garner and co-workers for $C_{34}H_{70}$, multiplying by the molecular weight ratio, 450/478, and calculating equal distances below the melting points of the two substances. The curve has not been extended very far down on account of the uncertainties involved, the most serious of which is lack of knowledge concerning the change in specific heat of the liquid. The calculation must be regarded as purely tentative and will be corrected in the near future by aid of a direct calorimetric investigation of dicetyl now under way.

The ideal solubility, on the basis of this preliminary calculation, appears to be somewhat less than the observed solubility in the three solvents, although the discrepancy is not great. Most striking, however, is the agreement between the curves for butane and heptane, themselves differing considerably in length of chain. The smaller solvent power of propane is doubtless to be expected, partly, at least, on account of pressure effects not accounted for.

It is worth mentioning in this connection that the system benzene–diphenyl, which is similar in principle to the model here discussed, deviates only slightly from ideal behavior,[13] and that there are other systems composed of molecules of widely different volumes, such as sulfur, 136 cc. per mole, and iodine, 59 cc. per mole, of which this is also true. It may hardly be worth while to attempt a too close check of a pure volume effect because of the doubtful possibility of eliminating completely all differences in other factors, particularly molecular field strength.

Summary

The lattice of fixed points as a frame of reference for calculating the entropy of binary solutions is applicable only to pairs of molecular species of equal size or, at most, to molecules whose size and shape permit them to occupy a

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[9] W. E. Garner, K. van Bibber and A. M. King, *J. Chem. Soc.*, 1533 (1931).

[10] Y. Delcourt, *Bull. soc. chim. Belg.*, **40**, 284 (1931).

[11] L. Deffet, *ibid.*, **44**, 41 (1935).

[12] *Cf.* F. Simon, *Ann. Physik*, **68**, 241 (1922); W. F. Giauque and R. Wiebe, THIS JOURNAL, **50**, 2193 (1928); **51**, 1441 (1929).

[13] J. C. Warner, R. C. Scheib and W. J. Svirbely, *J. Chem. Phys.*, **2**, 590 (1934).

definite number of lattice points. If a solution of long paraffin molecules is somewhat idealized as a parallel arrangement, the number of possible interchanges is the same as it would be for spherical molecules of equal size in a point lattice. This leads to the entropy and free energy of an ideal solution. The rather meager experimental evidence supports the ideal character of such solutions.

BERKELEY, CALIF. RECEIVED FEBRUARY 15, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY, INDIAN INSTITUTE OF SCIENCE]

Vapor Phase Esterification Equilibria

BY S. K. KULKARNI JATKAR AND N. G. GAJENDRAGAD

A study of various papers[1] on the vapor phase esterification of alcohols and acetic acid would seem to indicate a high temperature coefficient on the basis of Sabatiers[1e] value of 70% at 300° and Edgar's[1h] figure of 97% at 53°, but the large possible error admitted by Edgar and the lack of precision in the data of earlier workers, leaves doubt as to the actual position of equilibrium at intermediate temperatures, especially in view of the agreement of the constants found by Frolich, Carpenter and Knox[1l] at 280–300° and Swietoslawski[1,i,j] at 75°. Parks and Huffman[2] have used these values in calculating the free energy of ethyl acetate, and obtained satisfactory concordance with estimates based on the third law, but in disagreement with results of other workers.

Swietoslawski and co-workers apparently did not correct for acetic acid polymerization nor for the activities of the compounds, both of which are appreciable at 75°. As to the high values of Frolich and coworkers, the only probable explanation for them is that some of the catalyst must have been in the cooler portion of their apparatus. On account of the high temperature coefficient of the equilibrium constant, the reaction products must be "frozen," and it seems probable that temperature errors may account for some of the other experimental discrepancies.

Figure 1 shows a plotting of log Kp against $1/T$ of the results of various workers, and harmonizes out all the values from 77 to 300° except those of Frolich, *et al.* The fact that a straight line can be drawn among most of the values shows that ΔC_p for this reaction is practically zero, and it is only coincidence that our values lie between those extrapolated from the results of others. The acetic acid dissociation and the compressibility corrections are too small to affect our results. Perhaps the dotted line drawn through the more accurate values of Essex and Clark represent the true position of affairs.

The object of the present work was to obtain results with silica and potassium alum catalysts and discuss them in the light of the work of other investigators.

Experimental

The previously described method[1b] was used, in which the alcohol–acid mixture is allowed to flow drop by drop into a copper tube vaporizer (not attacked by acetic acid above 180°), superheated, passed through the catalyst tube and the products condensed in a test-tube in a freezing mixture.

The silica catalysts were prepared from iron-free water glass, analyzing for an $Na_2O:SiO_2$ ratio of 1.07:1 and 30.8% of water. The silicate solution was allowed to flow dropwise into 1.5 liters of vigorously stirred dilute hydrochloric acid contained in a 4-liter beaker, until the resulting gel set and stirring was impossible. The gel was then broken up, washed well with hot distilled water and dried in various ways, the most active catalyst being produced in partial vacuum. For this catalyst the optimum temperature was 260°, and the initial and final total acids agreed well except at temperature extremes.

Esterification of Ethyl Alcohol and Acetic Acid with Silica Catalyst at 260°.—For various rates of passage the esterification limit was found to be 75% for the 1:1 mixture and 91% for the 2:1 mixture (Table I).

The equilibrium also was studied from the hydrolysis side, pure ethyl acetate being taken into the buret and ester vapor saturated with water passed through the superheater into the reaction chamber, the proportion of water being

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[1] (a) Jatkar and Watson, *J. Indian Inst. Sci.*, **9A**, 71 (1926); (b) Gajendragad, Jatkar and Watson, *ibid.*, **15A**, 59 (1932); (c) Gajendragad and Jatkar, *J. Indian Chem. Soc.*, **12**, 486 (1935); (d) H. T. Briscoe and F. E. Dolian, *Proc. Indiana Acad. Sci.*, **42**, 101 (1933); *C. A.*, **27**, 5719 (1933); (e) Sabatier and Mailhe, *Compt. rend.*, **152**, 358, 494 (1911); (f) Mailhe and Godon, *Bull. Soc. Chim.*, [4] **29**, 101 (1921); (g) Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924); (h) Edgar and Schuyler, THIS JOURNAL, **46**, 64 (1924); (i) Swietoslawski and Poznanski, *Compt. rend.*, **184**, 92 (1927); (j) Swietoslawski and Salcewicz, *ibid.*, **199**, 130 (1934); (k) Gajendragad, *Proc. 15th Indian Sci. Cong.*, 148 (1928); (l) Frolich, Carpenter and Knox, THIS JOURNAL, **52**, 1565 (1930); (m) Jatkar and Gajendragad, "Proc. Indian Sci. Cong., Nagpur," 1931; (n) Tidwell and Reid, THIS JOURNAL, **53**, 4353 (1931); (o) Essex and Clark, *ibid.*, **54**, 1290 (1932).

[2] Parks and Huffman, "Free Energy of Organic Compounds," Reinhold Publishing Corporation, New York, N. Y., 1935, p. 174.

TABLE I

SILICA CATALYST, 48 G. AT 260°

EtOH:AcOH = 1:1

Expt.	142	143	132	133	140	141
Rate	18	18	10	10	5	5
Esterification, %	45.0	45.5	61.9	63.0	74.7	75.3

EtOH:AcOH = 2:1

Expt.	154	155	159	160	157	158
Rate	8.0	8.0	5.9	5.6	4.0	3.8
Esterification, %	79.1	79.6	83.8	88.7	88.0	91.0

controlled by the humidifier temperature. The reaction should produce equivalent quantities of acid and alcohol, so the free acid and total acid per gram of product were determined, the alcohol assumed to be equal to the free acid and the water found by difference (Table II).

TABLE II

REVERSE REACTION: 48 G. OF SILICA CATALYST AT 260°

	Init. compn. mixt.			Compn. prod., mole %				
Expt.	Ester	Water	Rate	Ester	Water	Alc. = Acid	Kp	Conv., %
146	67	33	8	57.0	23.4	9.8	14	79.9
147	66	34	5	55.5	22.6	10.9	10	76.2
148	66	34	5	55.5	22.6	10.9	10	76.2
149	68	32	5	57.5	21.3	10.6	10	76.2
175	81	19	6.2	69.2	6.6	12.0	3.2	
176	74	26	6.2	63.0	15.1	10.9	7.9	73.6
177	72	28	6.0	61.5	17.3	10.6	9.5	75.6
178	74	26	6.0	62.4	15.2	11.2	7.6	73.2
179	73	27	4.5	62.2	16.0	10.9	8.4	74.4
180	73	27	3.4	62.2	16.0	10.9	8.4	74.4
197	57	43	20	45.5	31.0	11.7	10	76.2
198	54	46	20	42.1	34.9	11.5	10	76.1

The calculated equilibrium constants expressed in terms of percentage esterification of an equimolecular alcohol-acid mixture are given in the last column. Our results and those of others show the necessity of slow passage for equilibrium. Plotting the percentage conversion in the last column against rate of passage for direct, reverse and "equilibrium" runs, and extrapolating from different rates of passage, gives values for Kp at zero rate, complicated by difficulty in maintaining the activity of the catalyst constant during a series. The curve for expts. 146–149, carried out with fresh catalyst and initial mixtures of 2:1 ester and water, gives 75% as the limit for the reverse reaction. Experiments 175–180, with another catalyst and a 3:1 mole mixture of ester and water gave 74.4% conversion for an equimolecular mixture. Experiments 197–198 were made with 60 g. of fresh catalyst and a 1:1 mixture of ester and water, the result showing that even with the passage of 20 g. per hour equilibrium is attained within 1%. Some experiments to find the limit of the reverse reaction have been carried out by passing over the catalyst at various rates synthetic mixtures corresponding to the constants 4, 6, 8, 10 and 14 (Table III).

TABLE III

QUADRUPLE MIXTURES WITH 48 G. OF SILICA CATALYST AT 260°

		Composition of product, mole %					
Expt.	Rate	Ester	Water	Alc.	Acid	Kp	Conversion, %
		33.7	31.6	17.0	17.6	4	
191	23	37.1	35.8	13.4	13.7	7	72.4
189	16	37.9	35.8	12.8	13.5	8	73.7
188	15	37.0	37.8	12.7	12.4	9	75.0
184	10	39.3	37.1	11.5	12.1	10	76.2
185	10	36.7	36.3	13.4	13.6	7	72.8
186	9.5	39.3	35.8	12.2	12.6	9	75.0
187	9	38.6	37.4	11.8	12.2	10	76.2
183	9	39.8	36.6	11.3	12.2	10	76.2
190	5	37.8	37.7	12.9	13.5	8	73.7
		37.8	36.0	12.8	13.4	8	
93	20	39.3	37.0	11.5	12.2	10	76.2
195	18	38.6	37.1	12.0	12.4	10	76.2
196	12	38.9	37.2	11.7	12.2	10	76.2
194	10	37.4	37.5	12.6	12.5	9	75.0
		37.0	42.5	10.3	10.3	14	
201	20	35.5	41.6	11.4	11.5	11	77.1
202	5	36.7	39.8	11.8	11.8	10	76.2
		36.1	40.1	11.9	11.9	10	
210	12	39.7	44.2	13.4	13.4	9	75.0
211	6	34.3	41.6	12.0	12.0	9	75.0
		65.0	12.5	11.0	11.5	6	
212	20	65.3	12.0	11.1	11.7	6	71.0
213	10	64.4	13.7	10.9	11.0	7	72.5
		68.2	12.0	9.7	10.1	8	
214	20	67.3	13.1	9.3	10.3	9	75.0
215	10	68.2	12.0	9.7	10.1	8	74.1

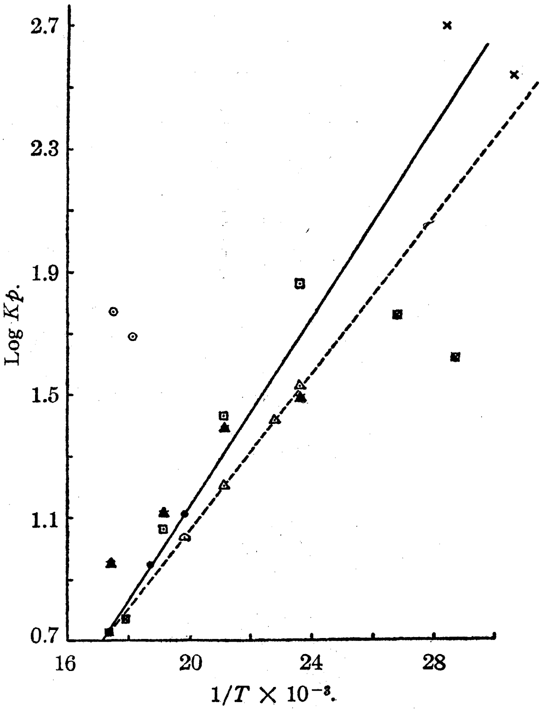


Fig. 1.—Esterification equilibria in the vapor phase: ■, Sabatier and Mailhe, 1911; ⊠, Mailhe and Godon, 1921; □, Milligan, Chappell and Reid, 1924; ▲, Tidwell and Reid, 1931; △, Essex and Clark, 1932; ○, Frolich and co-workers, 1930; ⊗, Swietoslawski and co-workers, 1929, 1934; ×, Edgar, 1924; ●, SiO_2, ⌓, alum, authors, 1931, 1936.

The results in Table III on graphical extrapolation show that the limit is reached when the product composition is such that $C_{\text{ester}}C_{\text{H}_2\text{O}}/C_{\text{alc.}}C_{\text{acid}} = 9$ approximately. The equilibrium point does not change with variation of water content in the initial mixture, the value of Kp remaining sensibly the same in expts. 212–216 with an ester/water ratio of 5, and in expts. 182–191 where the ratio was 1.

Esterification with Silica Gel at 230°.—Various silica catalysts were tested at 230°, but they were found to be relatively inactive, giving no limit of esterification. The maximum conversion was 73%, and in hydrolysis experiments with initial mixtures of 2 moles of ester to 1 mole of water the lowest value was 80% and that extrapolated from different flow rates was 78%. A mixture of ester, water, alcohol and acid in the mole ratio of 30.2:38.7:10.1:15.6 corresponding to $Kp = 4$, was passed at 10 cc. per hour over the catalyst and the mole ratio of the product was 34.9:42.8:11.6:10.8, corresponding to an equilibrium constant of 11.7.

It is evident that silica gel is not sufficiently active at 230°, and as the equilibrium is less favorable for ester at higher temperatures, various other catalysts have been studied, potassium hydrogen sulfate being the best (results to be published elsewhere).

Esterification with Potassium Alum Catalyst at 230°.—The optimum esterification temperature for this catalyst, prepared as described by Jatkar and Watson,[1a] is 230°, just as for ether dehydration of methyl and ethyl alcohols.[1a,b] Some experiments (Table IV) were made passing equimolecular mixtures of ethyl alcohol and acetic acid at 10 cc. per hour over 100 g. of potassium alum catalyst in the space which previously contained 50 g. of silica. Esterification begins at 160–170°, the same temperature at which alcohol begins to dehydrate if passed alone.

TABLE IV

Expt.	48	49	50	51	52	53	54
Temp., °C.	185	200	210	220	230	240	250
Esterification, %	14.0	33.5	41.2	53.2	62.7	60.6	61.9

Experiments also were run to ascertain the maximum esterification at various rates, using a mixture of alcohol 47.6 moles, acetic acid 47.4 moles and water 4.94 moles. In all the experiments (Table V) the initial and final total acid agreed, and the results show that a limit is reached easily, in contrast with silica catalysts.

TABLE V

POTASSIUM ALUM CATALYST, 105 G. AT 230°

Expt.	9	10	19	13	14	15	20	21
Rate	25.0	25.0	20.0	10.0	10.0	5.0	3.8	2.4
Esterif., %	63.7	61.8	64.7	65.5	65.0	65.5	61.5	63.5
Expt.		57	58	55	56	59	60	
Rate		20	20	10	10	5	5	
Esterif., %		64.0	63.7	65.3	64.6	66.1	64.8	

The hydrolysis of ethyl acetate has been studied with the same catalyst in the same apparatus. For rates of 20–10 g. per hour the value of Kp was about 10 (Table VI), while with slower rates hydrolysis went further and gave $Kp = 5$. This was due to ether formation in a side reaction. No ether could be detected in either direct or reverse reactions at rates of 10–20 cc. per hour.

Table VI

Experiment		25	24	23	28
Rate, g.		20	14.6	13	13
Mole % compn. prod.	Ester	32.2	34.1	26.9	22.5
	Water	43.7	42.4	48.4	55.1
	Alc. = acid	12.0	11.7	12.3	11.5
Kp		9.9	10.7	8	9.9

Taking the equilibrium value $Kp_{\text{ether}} = C_{\text{Et}_2\text{O}}C_{\text{H}_2\text{O}}/C^2_{\text{EtOH}} = 7$ at 230° found by Jatkar and Watson for the ether reaction and the limiting esterification value of a 1:1 alcohol-acetic acid mixture as 67% (the lower observed value 65% being due to initial water) the equilibrium constant for ester formation at 230° calculates to be 10.7, in good agreement with the figure found by extrapolation of the results of Essex and Clark.

Acknowledgment.—Our thanks are due to Dr. H. E. Watson for his keen interest during the progress of this work.

Summary

Measurements have been made on the vapor phase esterification equilibria of ethyl alcohol and acetic acid at 230 and 260°, using silica gel and potassium alum as catalysts, and the results found to correspond to 77 and 75% conversion of the equimolecular mixtures.

Although potassium alum is far more active than silica gel for esterification, the lower limit with this catalyst is due to the simultaneous establishment of ether equilibrium.

BANGALORE, INDIA RECEIVED AUGUST 4, 1936

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

A New Thiazane Synthesis

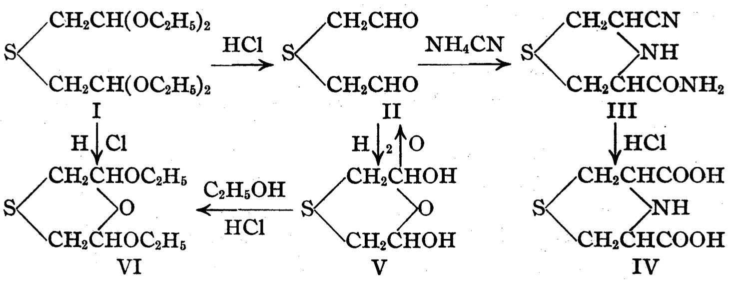
BY ROBERT D. COGHILL

For the purposes of some other research it was desired to obtain a sample of thiazane-3,5-dicarboxylic acid (IV). As this represents a new type of thiazane derivative it was necessary to devise a method of entering the series. It was found possible to do this by means of Strecker's well-known cyanohydrin synthesis.

Acetalyl sulfide (I) was prepared by a modification of Fischer's[1] method. In passing it should be mentioned that this substance is apparently what Curtius[2] prepared and described as mercaptoacetal. The acetalyl sulfide can be hydrolyzed by means of dilute hydrochloric acid to thiodiacetaldehyde (II). This aldehyde cannot be isolated as such but apparently exists in solution in equilibrium with 3,5-dihydroxythioxane (V), which is very reminiscent of the relationship existing between succinic dialdehyde and furan. In this case the 3,5-dihydroxythioxane can be isolated by concentrating the solution. The diethyl acetal of this substance, 3,5-diethoxythioxane (VI), can also be prepared from acetalyl sulfide as noted by Clarke and Smiles.[3]

When a solution of thiodiacetaldehyde is treated with ammonium cyanide, a somewhat complicated reaction sets in, the net result of which is the formation of the amide of 3-nitrilothiazane-5-carboxylic acid (III). Whether the Strecker reaction proceeds with the open chain form of the aldehyde, or whether the ammonium cyanide reacts with the dihydroxythioxane, is problematical. At first thought it seems unreasonable that only one of the nitrile groups should be hydrolyzed during the Strecker reaction, but somewhat similar reactions are not unknown in the chemical literature, and as this substance is quite insoluble and precipitates from the reaction mixture over a period of twenty-four hours, solubility considerations may well be the governing factors.

The nitriloamide resulting from the Strecker reaction can be transformed into the desired thiazane-3,5-dicarboxylic acid by means of concentrated hydrochloric acid. The synthesis can be represented as follows



Experimental

Acetalyl Sulfide.—This substance was prepared from bromoacetal and potassium sulfide as described by Fischer,[1] except that the reaction, instead of being autoclaved, was refluxed overnight. The yield was 75%. When potassium hydrosulfide was used instead of the sulfide, hydrogen sulfide was evolved copiously and acetalyl sulfide was obtained as above, except in smaller yield. Curtius[2] describes the product of this latter reaction as mercaptoacetal.

Thiodiacetaldehyde and 3,5-Dihydroxythioxane.—Twenty-six grams of acetalyl sulfide was vigorously shaken with 100 cc. of 0.5% hydrochloric acid at a temperature of 40–50° until solution was practically complete. The material now gave a very strong, nearly blue color to Schiff's reagent. A small amount of norite was then added and the solution filtered. The filtrate was evaporated to a volume of 50 cc. *in vacuo* at room temperature and then cooled in an ice-bath. The material separated as white needles, a second crop bringing the yield to 11.8 g., or nearly the theoretical. For analysis the material was dried in a vacuum desiccator over sulfuric acid.

Anal. Calcd. for $C_4H_8O_3S$: S, 23.5. Found: S, 22.9.

3,5-Dihydroxythioxane melts at 73° and is soluble in water at room temperature. Its solution imparts a deep bluish purple color to Schiff's reagent, entirely different from the color given by other aldehydes. When placed on the skin it imparts a deep brown stain impossible to remove. It has a very characteristic odor. When its solution is treated with saturated salt solutions or a trace of alkali, or even when the solid is kept in the dry state, it polymerizes or condenses to a water insoluble material. Due to this property it was always used in dilute aqueous solution just after hydrolysis from the acetal.

When warmed with alcohol and a trace of hydrochloric acid, it is transformed quantitatively into 3,5-diethoxythioxane, VI.

The Amide of 3-Nitrilothiazane-5-carboxylic Acid.—Fifty-three grams of acetalyl sulfide was hydrolyzed as above with 300 cc. of 0.5% hydrochloric acid. After

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(1) Fischer, *Ber.*, **42**, 1070 (1909).

(2) Curtius and Kyriacou, *J. prakt. Chem.*, [2] **95**, 370 (1917).

(3) Clarke and Smiles, *J. Chem. Soc.*, **95**, 992 (1909).

filtration of the hydrolysate it was concentrated *in vacuo* at room temperature to a volume of 100 cc. To the cooled concentrate was then added 11.2 g. of liquid hydrogen cyanide and the mixture was allowed to stand for ten minutes, after which an aqueous solution of 7.0 g. of ammonia was added slowly with stirring. The solution was then placed in the ice-box overnight. The reaction product was filtered off and recrystallized from 95% alcohol, in which it is sparingly soluble, to yield a crop of yellow needles. The yield is 17 g. or 50%. It melts with decomposition at 192°.

Anal. Calcd. for $C_6H_9ON_3S$: C, 42.1; H, 5.25; N, 24.5; S, 18.7. Found: (Schoeller) C, 42.2; H, 5.44; N, 23.5; S, 18.7.

This substance is insoluble in cold water and all organic solvents tried except boiling alcohol, but soluble in concentrated hydrochloric or sulfuric acid. When boiled with concentrated sodium hydroxide it gives off exactly two-thirds of its nitrogen as ammonia. When boiled with 0.05 *N* sodium hydroxide, one-third of the nitrogen appears as ammonia in twenty minutes. The second nitrogen is much slower to hydrolyze, only half of it appearing as ammonia in two hours. This behavior, coupled with its high insolubility, is interpreted as confirming the assigned structure.

Thiazane-3,5-dicarboxylic Acid.—Ten grams of the above nitriloamide was refluxed for three hours with concentrated hydrochloric acid. At the end of that time it was evaporated to dryness on a water-bath, taken up in water and made *just* alkaline to Congo red with ammonia, whereupon the thiazane-3,5-dicarboxylic acid came out in white needles which can be recrystallized from water and which contain one mole of water of crystallization. The yield was 6 g. or 56%. When heated it first decrepitates then melts with decomposition at 253–254°.

Anal. Calcd. for $C_6H_9O_4NS{\cdot}H_2O$: H_2O, 8.6; C, 34.5; H, 5.26; N, 6.7; S, 15.3. Found: (Schoeller) H_2O, 8.7; C, 34.4; H, 5.35; N, 6.3; S, 15.3.

Summary

A new application of the Strecker reaction, ring closure, has been used to enter the thiazane series.

Thiazane-3,5-dicarboxylic acid has been synthesized by means of this method. This substance can serve as a starting point for the synthesis of many new thiazane derivatives.

NEW HAVEN, CONN. RECEIVED NOVEMBER 10, 1936

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

White Oak Holocellulose[2]

BY CARROLL D. BIRD AND GEO. J. RITTER

Holocellulose, the carbohydrate fraction in wood freed of its extraneous materials, has proved within the last three years a promising material for the study of the composition of wood.[3,4] It is similar in composition to the wood fraction, "skelettsubstanz,"[5] that is isolated by means of an aqueous solution of pyridine and chlorine dioxide.

Since the results on holocellulose from maple[3] and spruce[4] were published, others have been collected on the holocellulose from white oak. They are considered in the present paper.

Materials Used.—White oak sawdust (60–80 mesh) was used in this study. It was first extracted consecutively with alcohol, alcohol–benzene solution, and hot water to remove extraneous materials.

Alcohol–pyridine solution, consisting of 85 parts of 95% alcohol and 15 parts of pyridine (by volume), was used as the solvent.

A bleach solution was employed that was made by dissolving commercial chlorinated lime in distilled water. The supernatant liquor was removed from any undissolved residue by filtration and diluted so as to contain 1.6% of available chlorine. It was cooled to 10° and was made just acid to litmus by means of acetic acid immediately before using.

Isolation of Holocellulose.—The method developed by Ritter and Kurth[3] was employed for the isolation of holocellulose. Briefly, it consists of repeated alternate treatments of the wood with gaseous chlorine and alcohol–pyridine solution.

Four chlorinations were required to remove the maximum amount of lignin from the wood before carbohydrates began dissolving as was shown by determining[6] the lignin content of a control sample. In general, at this stage of delignification about 1.0% of lignin still remained in the residue. The residual lignin was removed by means of the bleaching solution at 10°.

Physical Properties of White Oak Holocellulose.—Unbleached white oak holocellulose is grayish tan in color; the bleached material is light-cream. It can be bleached

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[1] Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

[2] To be presented before the Cellulose Division of the American Chemical Society at Chapel Hill, N. C., April 12, 1937.

[3] G. J. Ritter and E. F. Kurth, *Ind. Eng. Chem.*, **25**, 1250 (1933).

[4] E. F. Kurth and G. J. Ritter, THIS JOURNAL, **56**, 2720 (1934).

[5] E. Schmidt, K. Meinel and W. Jandebeur, *Cellulosechem.*, **13**, 129 (1932).

[6] G. J. Ritter and J. H. Barbour, *Ind. Eng. Chem., Anal. Ed.*, **7**, 238 (1935).

white but in doing so a small percentage of the acetyl groups is apt to be removed.

White oak holocellulose resembles the untreated wood structurally in that the fibers cling together. The clinging tendency of the fibers indicates the presence of carbohydrate material in the middle lamella and confirms findings by Bailey.[7] These physical properties are similar to those of maple and spruce holocellulose.[3,4]

Chemical Composition of Holocellulose.—The chemical composition of the holocellulose was determined by the following analyses: lignin was determined by the 72% sulfuric acid method,[6] methoxyl by the Zeisel method,[8] carbon dioxide by the 12% hydrochloric acid method,[9] acetyl by the toluene-sulfonic method[10] and pentosans by Tollens' method.[8]

The following three materials were analyzed by one or more of the foregoing methods: (1) white oak sawdust freed of its extraneous materials; (2) bleached holocellulose isolated from Material 1; (3) lignin isolated from Material 1 by means of the 72% sulfuric acid method. Table I shows the yields and composition of the three materials. Table II records the composition of the materials calculated on the basis of the extractive-free wood so as to reveal the proportion of the substituent groups in each of the three materials.

TABLE I

YIELDS AND RESULTS OF ANALYSIS OF EXTRACTIVE-FREE WOOD, HOLOCELLULOSE AND LIGNIN

Yields of materials based on oven-dry weight of extracted wood; results of analysis based on oven-dry weight of materials.

Material	Yields, %	Lignin 72% Sulfuric acid, %	Methoxyl, %	Carbon dioxide, %	Acetyl, %	Pentosans, %
Extracted white oak wood	100.0	23.40	6.44	1.20	2.37	18.70
White oak holocellulose	75.6	0.00	1.64	1.56	3.07	23.40
White oak lignin	23.4	...	22.44	..	..	...

White oak holocellulose is free from lignin (Table I). Its methoxyl content is about 25% of that of the extracted wood; it liberates considerably higher percentages of carbon dioxide than the wood; and it contains higher percentages of acetyl groups and pentosans than the wood. The carbon dioxide evolved from the holocellulose is believed to be a decarboxylation product of uronic acids. These acids and high percentages of pentosans render holocellulose especially prone to hydrate quickly in a pulp beater. As a result, it is converted to a stuff excellent for glassine paper by a sixty-minute processing treatment as compared with a ten-hour treatment for a refined pulp.

TABLE II

COMPOSITION OF EXTRACTED WOOD, HOLOCELLULOSE AND LIGNIN

Results based on oven-dry weight of extracted wood.

Material	Yields, %	Lignin 72% Sulfuric acid %	Methoxyl, %	Carbon dioxide, %	Acetyl, %	Pentosans, %
Extracted white oak wood	100.0	23.40	6.44	1.20	2.37	18.70
White oak holocellulose	75.6	0.00	1.23	1.18	2.32	17.70
White oak lignin	23.4	...	5.25	..	..	...

One per cent. of the holocellulose was lost during the isolation procedure (Table II), the sum of the holocellulose and the lignin being 99.0% (75.6 + 23.4 = 99.0). The loss occurs in pentosans as is shown in the last column. About 20.0% of the methoxyl groups are located in the holocellulose and 80.0% in the lignin. Within experimental error the results indicate that the carbon dioxide forming material and the acetyl groups of the wood are located in the holocellulose. These results on the location of the methoxyls, carboxyls and acetyls, are in agreement with those on maple and spruce holocellulose.[3,4]

Summary

White oak holocellulose has been isolated by means of alternate treatments with chlorine gas and alcohol–pyridine solution. It has physical properties similar to those of holocellulose from maple and spruce reported previously. Its substituent groups are also distributed similarly to those in maple and spruce; about 20% of the methoxyls and all the carboxyls and the acetyls are located in the white oak holocellulose.

MADISON, WIS. RECEIVED FEBRUARY 23, 1937

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(7) A. J. Bailey, *Ind. Eng. Chem., Anal. Ed.* **8** (1), 52 (1936).

(8) M. W. Bray, *Paper Trade J.*, **87**, 59 (1928).

(9) A. D. Dickson, H. Otterson and K. P. Link, THIS JOURNAL, **52**, 775 (1930).

(10) K. Freudenberg, *Ann.*, **433**, 230 (1923).

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

The Enolizing Action of Methylmagnesium Iodide upon Hindered Ketones[1]

BY LEE IRVIN SMITH AND CYRUS GUSS[2]

The reaction between ketones and Grignard reagents most frequently consists in addition of the reagent to the carbonyl group. However, when the carbonyl group or the Grignard reagent is hindered by the accumulation of substituents near the functional group, speed of the addition reaction is reduced greatly, and under these circumstances time is available for other slower reactions to occur. The chief of these slower reactions are enolization, condensation and reduction.[3] Acetomesitylene has been studied rather extensively as an example of a hindered ketone in which the ordinary reactions involving addition to the carbonyl group are decreased in velocity to the point at which the slower, "abnormal" reactions make themselves felt. Thus the oxime cannot be made by the ordinary procedures;[4] the ketone is completely resistant to the action of alkalies, but is cleaved to the hydrocarbon (mesitylene) and acetic acid by the action of phosphoric acid,[5] in contrast to the behavior of acetophenone, which is cleaved to benzoic acid; and the ketone does not undergo the haloform reaction.[6]

Kohler, Stone and Fuson[7] using their "Grignard machine," found that acetomesitylene was completely enolized by methylmagnesium iodide, giving an iodomagnesium enolate together with an equivalent amount of methane, a result which was verified in a more extensive study of the reaction by Kohler and Baltzly.[4d] That enolization of ketones by Grignard reagents is primarily a function of hindrance in the ketone and that branching of the chain in the reagent is of relatively minor importance in this reaction, was shown by Kohler and Thompson.[8]

In order to extend and amplify the information on enolization of hindered ketones by Grignard reagents, the behavior of thirteen aceto- and diacetopolymethylbenzenes toward methylmagnesium iodide has been examined. The results are given in Table I.

The compounds were dissolved in xylene and analyses were made in a "machine" built essentially after the pattern of the one used by Kohler and his collaborators[7,9] and the procedure was essentially that used by them. The monoacetyl compounds were fairly easily handled, but the diacetyl compounds gave rise to complications due to the insolubility of the iodomagnesium derivative in the solvent. In such cases, the amount of xylene, as well as the time during which the reaction mixture was heated, had to be increased considerably before consistent results could be obtained. When water was added in the second part of the analysis it was also necessary to prolong the time of heating. Moreover, cautious shaking of the reaction chamber during both the first part of the analysis and the later decomposition by water was absolutely necessary. A correction factor, due to gas (nitrogen) dissolved in the reagent and to moisture which could not be removed from the apparatus, had to be introduced into the calculations. The correction, experimentally determined, amounted to 1.52 cc. Consistent values for the amount of

TABLE I

GRIGNARD ANALYSES OF ACETOPOLYMETHYLBENZENES

Ketone	Active H moles per mole of ketone	Moles of reagent added per mole of ketone
Acetophenone	0.025	1.025
Aceto-*m*-xylene	.05	1.02
Acetomesitylene	1.03	0
5-Acetopseudocumene	0.25	0.79
Acetodurene	.97	.04
Acetoisodurene	.94	.07
Acetoprehnitene	.75	.27
Acetopentamethylbenzene	.93	.01
Diaceto-*m*-xylene	.16	1.82
Diacetomesitylene	1.82	0.26
Diacetopseudocumene	1.66	.44
Diacetodurene	1.62	.54
Diacetoisodurene	1.72	.48
Diacetoprehnitene	1.68	.46

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[1] Polymethylbenzenes. XVI. Paper XV, THIS JOURNAL, **58**, 1 (1936).

[2] Abstracted from a thesis by Cyrus Guss, submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science, July, 1936.

[3] Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929).

[4] (a) Baum, *Ber.*, **28**, 3207 (1895); (b) Meyer, *ibid.*, **29**, 830 (1896); (c) Feith and Davies, *ibid.*, **24**, 3546 (1891); (d) Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932).

[5] Klages and Lickroth, *Ber.*, **32**, 1549 (1899).

[6] Fuson and Walker, THIS JOURNAL, **52**, 3269 (1930).

[7] Kohler, Stone and Fuson, *ibid.*, **49**, 3181 (1927).

[8] Kohler and Thompson, *ibid.*, **55**, 3822 (1933).

[9] Kohler and Richtmyer, *ibid.*, **52**, 3736 (1930).

enolization were obtained readily, but values for the amount of addition varied, often by as much as 5% especially for the diaceto compounds. At least three analyses of each ketone were made; the figures given are average values. Acetophenone is included in the table for comparison.

The results given in Table I show that all of the monoketones having methyl groups in both ortho positions to the carbonyl group are 100% enolized by methylmagnesium iodide. When only one ortho position is substituted by a methyl group the extent of enolization apparently is affected by the number of methyl groups elsewhere in the ring as shown by aceto-*m*-xylene, acetopseudocumene and acetoprehnitene which are enolized to the extent of 5, 24 and 75%, respectively. Among the diaceto compounds, enolization does not reach 100%, and diaceto-*m*-xylene is only 8% (per carbonyl group) enolized. Because of this result, it was thought that this compound might possibly be 4,6-diaceto-*m*-xylene, although the arguments of Meyer and Pavia[10] as well as those of Klages and Lickroth[5] (p. 1562) indicate quite strongly that the substance is 2,4-diaceto-*m*-xylene. Diacetomesitylene shows the greatest amount of enolization (90% per carbonyl group) of any of the diketones. The other five diketones are 80–85% enolized by the reagent; the degree of enolization is apparently affected but little, if any, by the relative positions of the two acetyl groups.

The authors are greatly indebted to Dr. A. F. Thompson, Jr., for suggestions and criticisms with reference to the Grignard analyses.

Experimental Part[11]

The monoketones were prepared by the Friedel–Crafts synthesis from the hydrocarbons (1 mole), acetic anhydride (1.2 moles) and aluminum chloride (2.2 moles) in carbon bisulfide (400 cc.), according to the general procedure of Noller and Adams.[12] The products all distilled at nearly constant temperatures, except for small foreruns of hydrocarbons and some high boiling residues. The latter were worked up for diaceto compounds. The monoketones were all fractionated twice; in addition, acetodurene was crystallized from ether, and acetopentamethylbenzene from methyl alcohol.

For the diketones, the procedure was much the same, but using, per mole of hydrocarbon, 6 moles of aluminum chloride, 2.3 moles of acetic anhydride, and an amount of carbon disulfide sufficient to keep the reaction mixture fluid enough to stir well (200–500 cc.). The monoketones were removed from the products by fractionation and the residue was then distilled practically to dryness. The boiling points of the second fraction covered a wide range, but the distillate consisted almost entirely of the diketones which were crystallized from high boiling ligroin (A) or ether (B). Tables II and III show the physical constants and yields.

TABLE II

PREPARATION OF MONOKETONES

Ketone	Hydrocarbon used, moles	Yield, g.	Yield, %	B. p., °C.	Mm.
4-Aceto-*m*-xylene	1.0	80	54	113	18[a]
Acetomesitylene	0.5	43	72	121–123	18[b]
5-Acetopseudocumene	1.0	130	80	120–123	10[c]
Acetoisodurene	1.0	143	81	135–137	16[d]
Acetoprehnitene	0.5	58	70	122–124	8[e]
Acetodurene	1.0	138	80	129–131	10[d] m. p., 73°
Acetopentamethylbenzene[f]	1.0	153	80	144–145	8 m. p., 84°

[a] Klages, *Ber.*, **35**, 2248 (1902). [b] Dittrich and Meyer, *Ann.*, **264**, 138 (1891). [c] Klages and Allendorf, *Ber.*, **31**, 1005 (1898). [d] Baum and Meyer, *ibid.*, **28**, 3213 (1895). [e] Claus and Föhlisch, *J. prakt. Chem.*, [2] **38**, 231 (1888). [f] New. *Anal.* Calcd. for $C_{13}H_{18}O$: C, 82.11; H, 9.42. Found: C, 82.09; H, 9.21.

TABLE III

PREPARATION OF DIKETONES

Ketone	Hydrocarbon used, moles	Monoketone, g.	Diketone, g.	M. p., °C.
2,4-Diaceto-*m*-xylene	1.0	70	41	109 A[a]
Diacetomesitylene	1.0	70	38	44 A[b]
3,5-Diacetopseudocumene[e]	1.0	92	4.2	124 A
Diacetoisodurene	1.0	94	14	121 A[c]
Diacetodurene	0.5	15	11	178 B[c,d]
Diacetoprehnitene[f]	.5	35	8[g]	113 B

[a] Mayer and Pavia, *Ber.*, **29**, 2566 (1896). [b] Meyer, *ibid.*, **29**, 1413 (1896). [c] Baum and Meyer, *ibid.*, **28**, 3213 (1895). [d] Baum and Meyer, *ibid.*, **29**, 847 (1896). [e] New. *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.47; H, 7.85. Found: C, 77.24; H, 8.9. [f] New. *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.07; H, 8.26. Found: C, 77.38; H, 8.50. [g] A white solid (3 g.) melting at 164–174° was formed as a by-product in this preparation. It was diacetyldurene (m. p. 178°); mixed m. p. 170–178°. *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.07; H, 8.26. Found: C, 77.23, 77.08; H, 8.36, 8.12. This substance resulted from durene formed by action of aluminum chloride upon prehnitene during the prolonged, slow, diacetylation of prehnitene.

Summary

1. Thirteen aceto- and diacetopolymethylbenzenes, three of them new compounds, have been analyzed in the Grignard machine with regard to enolization by methylmagnesium iodide.

2. All of the diortho substituted monoketones were 100% enolized by the reagent.

3. The degree of enolization of the mono ortho substituted monoketones was increased by the presence of methyl groups in the meta and para positions.

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(10) Meyer and Pavia, *Ber.*, **29**, 2566 (1896).

(11) Microanalyses by J. W. Opie.

(12) Noller and Adams, THIS JOURNAL, **46**, 1889 (1924).

4. The diketones were only 80–90% enolized by the reagent; the relative positions of the two acetyl groups had little effect on the degree of enolization.

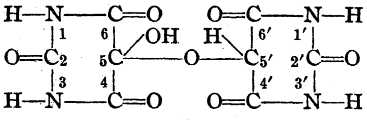
MINNEAPOLIS, MINN. RECEIVED FEBRUARY 23, 1937

[CONTRIBUTION FROM KENT CHEMISTRY LABORATORY, UNIVERSITY OF CHICAGO]

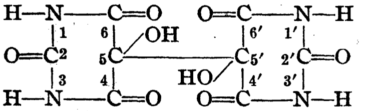
Studies in the Alloxantine Series[1]

BY DOROTHY NIGHTINGALE[2]

The formation and many of the reactions of alloxantine[3] can be explained by either the hemiacetal structure (I) of Piloty and of Slimmer and Stieglitz, or by the pinacol structure (II).



I



II

On the basis of the hemiacetal structure, it should be possible to prepare two isomeric methyl alloxantines and two unsymmetrical dimethyl alloxantines, namely, 1-methylalloxantine and 1′-methylalloxantine, and 1,3-dimethylalloxantine and 1′,3′-dimethylalloxantine. The first step, therefore, was to try to prepare the two possible monomethyl alloxantines, and then to determine by means of their hydrolytic products whether or not they maintained their identity. According to the pinacol formula they should be identical.

The 1-methylalloxantine can be prepared from methylalloxan and dialuric acid, and would be expected to yield these compounds on hydrolysis. Similarly, 1′-methylalloxantine should be formed by the union of alloxan and methyldialuric acid, and on hydrolysis should yield these same products. If the pinacol structure is correct, then either compound could yield a mixture of dialuric acid, methyldialuric acid, alloxan and methylalloxan. Tartar[4] concluded that the unsymmetrical dimethylalloxantines maintained their identity because the dimethyl murexides which he obtained from them gave dimethylalloxan and uramil, alloxan and dimethyluramil, respectively, when hydrolyzed with dilute hydrochloric acid. No further evidence was presented for their structures.

Alloxantine can be hydrolyzed with the following reagents and the hydrolytic products separated nearly quantitatively: (a) hydrochloric acid and the subsequent treatment of the solution with hydroxylamine hydrochloride, (b) hydroxylamine hydrochloride, (c) primary amines, (d) potassium acetate solution. When the mono or dimethyl alloxantines are used, however, this is no longer true. Solubilities are changed and yields lowered so that the hydrolytic products furnish little definite quantitative evidence as to probable structure.

Method (d) is useful for the isolation of only one hydrolytic product, namely, dialuric acid. According to Koech[5] freshly prepared potassium acetate solution hydrolyzes alloxantine to give alloxan and a quantitative yield of the slightly soluble potassium dialurate. The potassium salt of methyldialuric acid is very soluble in water, making this reaction of use only in detecting dialuric acid. A large excess of potassium acetate seems to be necessary for a quantitative yield of the potassium dialurate. With the theoretical amount, only a small quantity of potassium dialurate is precipitated. The reaction was applied to the methyl alloxantines with interesting results.

One rather unexpected result was observed, namely, the formation of potassium dialurate from 1′-methylalloxantine prepared from either 1-methyldialuric acid or its derivative 1-methyluramil. This result can be explained on the assumption that there is oxidation–reduction of methyldialuric acid by alloxan after hydrolysis.

According to Biilmann and Bentzon[6] alloxan-

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[1] Abstract of a portion of a dissertation presented by the author in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago in 1928. The investigation was carried out under the supervision of the late Professor Julius Stieglitz.

[2] Present address, University of Missouri, Columbia, Missouri.

[3] For a bibliography and brief discussion of the possible structures of alloxantine, see Davidson and Epstein, *J. Org. Chem.*, **1**, 305 (1936).

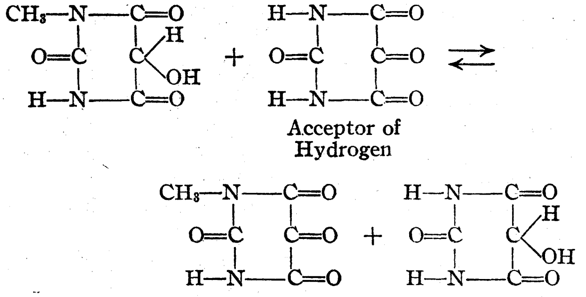
[4] H. V. Tartar, doctoral dissertation, University of Chicago, 1920.

[5] Koech, *Ann.*, **315**, 254 (1901).

[6] Biilmann and Bentzon, *Ber.*, **51**, 522 (1918).

tine is 78% dissociated in saturated aqueous solution into dialuric acid and alloxan. The extent and rate of dissociation of 1′-methylalloxantine should be somewhat the same as for alloxantine, since the methyl radical of the ureide group should not affect the group of atoms which are involved in the hydrolysis. In an aqueous solution of 1′-methylalloxantine there would be the equilibrium

1′-methylalloxantine $\rightleftharpoons$ 1-methyldialuric acid + alloxan



When potassium acetate is added, it reacts to form the slightly soluble potassium dialurate, more dialuric acid is formed to satisfy the equilibrium, and thus the 1′-methylalloxantine is destroyed completely. This is indicated by the fact that the potassium dialurate is precipitated slowly, completion of the reaction requiring several hours, whereas potassium dialurate is precipitated in a few minutes in excellent yield when either alloxantine or 1-methylalloxantine is hydrolyzed under the same conditions. This interpretation is in accordance with the hemiacetal formula for the alloxantines.

The acetyl and benzoyl derivatives of alloxantine prepared by Friedrich[7] from the corresponding acyldialuric acid and alloxan are stable compounds which melt without decomposition and are soluble in alcohol as well as in water. These facts suggested the possibility of preparing isomeric acyl methyl alloxantines which might have different melting points. The benzoyl derivatives were chosen because they do not hydrolyze as readily in aqueous solution as do the acetyl derivatives.

Benzoyldialuric acid and methylalloxan or dimethylalloxan reacted readily to form the corresponding benzoyl methyl or dimethyl alloxantines, but there was no evidence of any reaction between benzoylmethyldialuric acid and the alloxans.

Experimental

1-Methylalloxantine.—The compound can be prepared by either of the following methods: (1) the reaction between dialuric acid and methylalloxan, first proposed by Andreasch,[8] and later more carefully developed by Biltz and Heyn,[9] yielding about 30%; and (2) the reaction of uramil and methylalloxan in dilute hydrochloric acid solution, an application of the method recently described by Davidson and Epstein[3] but first developed by Tartar[4] for the unsymmetrical dimethyl alloxantines. The yield is nearly quantitative; hence this method, described below, was used more frequently.

Uramil (2.8 g.) and an excess of methylalloxan (4 g.) were added to 25 cc. of water containing 2 cc. of concentrated hydrochloric acid. The mixture was kept at a temperature of 50° for three hours, with the addition of a little water from time to time to keep the volume constant. The mixture was cooled and the colorless crystals collected on a filter, washed with water, alcohol and ether, and dried in a vacuum desiccator; yield 5 g.

Anal. Calcd. for $C_9H_8N_4O_8 \cdot 3H_2O$: N, 15.82. Found: (Kjeldahl) N, 15.72.

1′-Methylalloxantine.—Freshly prepared methyluramil (2.5 g.) and alloxan monohydrate (2.5 g.) were added to 20 cc. of water containing 2 cc. of concentrated hydrochloric acid. The mixture was kept at a temperature of about 60° for two and one-half hours, following the procedure given above; yield 4 g.

Anal. Calcd. for $C_9H_8N_4O_8 \cdot 3H_2O$: N, 15.82. Found: (Kjeldahl) N, 16.00.

Both compounds when recrystallized melt with decomposition at 226°, and soon turn red when exposed to air, especially if at all moist. The dried samples were kept in well-stoppered bottles in a desiccator. In order to avoid as far as possible oxidation–reduction during solution, the methylalloxantines for the hydrolysis experiments were not recrystallized. The compounds were recrystallized for analysis.

Hydrolysis of 1-Methylalloxantine.—The 1-methylalloxantine (3 g.) was dissolved in hot boiled water (75 cc.) and to this solution was added a solution of potassium acetate prepared as follows: 1.2 g. of potassium hydroxide was dissolved in 10 cc. of water and glacial acetic acid added drop by drop until the solution was just acid to litmus. Crystals of potassium dialurate began to separate rapidly as soon as the potassium acetate solution was added to the solution of 1-methylalloxantine. The solution was kept hot but not boiling, to prevent the precipitation of the difficultly soluble methylalloxantine. The precipitation was complete in about fifteen minutes. The crystals of potassium dialurate were collected on a filter, washed with alcohol and ether and dried in a vacuum desiccator; yield 1.17 g., theoretical 1.54 g.

Anal. Calcd. for $C_4H_3N_2O_4K$: N, 15.38. Found: (Kjeldahl) N, 15.37.

Hydrolysis of 1′-Methylalloxantine.—The 1′-methylalloxantine (3 g.) was hydrolyzed under the same conditions as 1-methylalloxantine. After standing for about

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[7] Friedrich, *Ann.*, **344**, 7 (1906).

[8] Andreasch, *Monatsh.*, **3**, 431 (1882).

[9] Biltz and Heyn, *Ber.*, **52**, 1310 (1919).

fifteen minutes, crystals of potassium dialurate began to form slowly. The precipitation required several hours for completion. As has already been pointed out, this relatively long interval is of theoretical significance. The yield of potassium dialurate was 1.35 g. The yield of salt possible if all of the 1′-methylalloxantine is converted into dialuric acid and methylalloxan is 1.54 g.

Anal. Calcd. for $C_4H_3N_2O_4K$: N, 15.38. Found: (Kjeldahl) N, 15.23.

The experiment was repeated several times, using 1′-methylalloxantine prepared by the Biltz–Andreasch directions as well as by Tartar's method, with the same results.

In support of the assumption that the formation of potassium dialurate from 1′-methylalloxantine is the result of intermolecular oxidation–reduction after hydrolysis, the following experiment was carried out. Methyldialuric acid (1.7 g.) was dissolved in hot water (60 cc.). To this solution was added the 10 cc. of potassium acetate solution prepared as described above. Alloxan monohydrate (1.6 g.) dissolved in water (15 cc.) was added at once. The solution was kept hot to prevent the precipitation of the methyldialuric acid. After a time, crystals began to separate and after several hours precipitation was complete. The crystals of potassium dialurate were collected on a filter and dried; yield 1.2 g., theoretical 1.8 g.

Anal. Calcd. for $C_4H_3N_2O_4K$: N, 15.38. Found: (Kjeldahl) N, 15.29.

Hydrolysis of the Unsymmetrical Dimethylalloxantines.—The unsymmetrical dimethylalloxantines were prepared in the same manner as the monomethyl alloxantines and were hydrolyzed with potassium acetate as described above. From 3 g. of 1,3-dimethylalloxantine an almost quantitative yield of 1.18 g. of potassium dialurate was obtained in a short time. A 2-g. sample of 1′,3′-dimethylalloxantine gave 0.65 g. of potassium dialurate, a 66% yield if all of the alloxan is reduced completely by dimethyldialuric acid to dialuric acid. This latter reaction proceeded slowly, as with 1′-methylalloxantine.

Benzoyl-1-methylalloxantine.—Friedrich's[7] directions were used to prepare benzoyldialuric acid. To a solution of the acid (1.5 g.) in 90 cc. of hot water, methylalloxan (1.5 g.) was added. Crystals separated when the solution was cooled and the beaker scratched. The benzoylmethyl alloxantine was collected on a filter, washed with water and finally with ether, and recrystallized from hot absolute alcohol. The yield was 0.72 g. of purified product which melted with decomposition at about 233°.

Anal. Calcd. for $C_{16}H_{12}N_4O_9$: N, 13.86. Found: (Kjeldahl) N, 13.93.

Benzoyl-1,3-dimethylalloxantine was prepared in the same manner from benzoyldialuric acid (1.5 g.) dissolved in 100 cc. of hot water and dimethylalloxan (1.7 g.). The yield was 1.3 g. The compound decomposed at 237°.

Anal. Calcd. for $C_{17}H_{14}N_4O_9$: N, 13.40. Found: (Kjeldahl) N, 13.41.

Benzoylmethyldialuric acid, a compound not described in the literature, was prepared as follows: 1-methyldialuric acid (5 g.) was added to 25 g. of benzoyl chloride and the mixture heated on an oil-bath for half an hour. A reaction began at about 120° with the evolution of hydrogen chloride. The methyldialuric acid went into solution at about 150°. Crystals separated when the mixture was cooled and the sides of the flask scratched. After standing for several hours, the crystals were collected on a Büchner funnel and as much of the benzoyl chloride as possible removed by suction. The compound was washed with ether until the odor of the acid chloride was no longer noticeable; yield 6 g., melting point 185–187°. Repeated recrystallization of the compound from hot water did not change its melting point.

Anal. Calcd. for $C_{12}H_{10}N_2O_5$: N, 10.68. Found: (Kjeldahl) N, 10.60.

The potassium salt of benzoylmethyldialuric acid was prepared from 2.5 g. of the acid dissolved in 70 cc. of 95% alcohol and a solution of 3.2 g. of potassium acetate in 30 cc. of alcohol. Colorless crystals separated rapidly when the two solutions were mixed. After standing some time, the crystals were collected on a filter, washed with alcohol and ether, and dried in a vacuum desiccator.

Anal. Calcd. for $C_{12}H_9N_2O_5K\cdot 1H_2O$: K, 12.30; N, 8.80. Found: K, 12.38; N, 8.83.

For the preparation of benzoyl-1′-methylalloxantine benzoylmethyldialuric acid (1.5 g.) was dissolved in 125 cc. of hot water and to this solution was added alloxan (0.5 g.). After several hours the crystals which separated (1.3 g.) were collected and dried. Their melting point was 185–187° and the melting point of a mixture of these crystals and benzoylmethyldialuric acid was also 185–187°.

Summary

1. The experimental evidence indicates that methylalloxantine may exist in the form of two isomers, as represented by the hemiacetal formula. In aqueous solution 1-methylalloxantine would dissociate into dialuric acid and methylalloxan, and when potassium acetate solution is added, potassium dialurate is precipitated rapidly. Similarly, 1′-methylalloxantine would yield methyldialuric acid and alloxan. The alloxan appears to be reduced slowly by the methyldialuric acid to dialuric acid, which is precipitated slowly as the difficultly soluble potassium dialurate. Similar results were obtained with 1,3-dimethylalloxantine and 1′,3′-dimethylalloxantine.

2. Methods are given for the preparation of the following compounds not described in the literature: benzoyl-1-methyldialuric acid, benzoyl-1-methylalloxantine, benzoyl-1,3-dimethylalloxantine.

COLUMBIA, MISSOURI

RECEIVED FEBRUARY 24, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FISK UNIVERSITY]

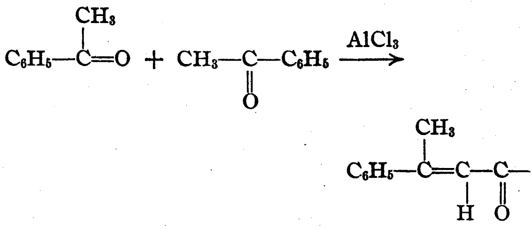
Reactions in the Presence of Metallic Halides. I. β-Unsaturated Ketone Formation as a Side Reaction in Friedel–Crafts Acylations

BY N. O. CALLOWAY[1] AND LOUIS D. GREEN

Often directions for the preparation of ketones by the Friedel–Crafts method from a hydrocarbon and an acid halide specify a reaction period of such length that hydrogen halide evolution ceases. These statements lead to ambiguous reaction conditions. A major difficulty is the problem of determining the point at which the hydrogen halide evolution stops. On the one hand, experience has shown that the reaction is seldom complete when there is no longer visible bubble formation at room temperature. On the other hand, it is not possible to discern bubble formation during reflux especially if low-boiling solvents are used.[2] Yet the ordinary test with ammonia shows *some* evolution of hydrogen halide *as long as the reaction mixture is refluxed.*

It has further been noted that prolonged reflux or extended reaction time actually decreases the yield of ketone beyond a certain period. This decrease in ketone is accompanied by an increase in the formation of high-boiling oxygen containing substances.

In an effort to find, if possible, a method that would minimize the loss of ketone by reaction subsequent to formation, it was observed in the synthesis of acetophenone that the residues consisted primarily of dypnone which had resulted from the condensation of two molecules of acetophenone.



$$C_6H_5-\overset{CH_3}{\overset{|}{C}}=O + CH_3-\underset{O}{\underset{\|}{C}}-C_6H_5 \xrightarrow{AlCl_3} C_6H_5-\overset{CH_3}{\overset{|}{C}}=\underset{H}{\underset{|}{C}}-\underset{O}{\underset{\|}{C}}-C_6H_5$$

Closer examination of this reaction revealed the fact that it is one that will take place to an extent approximating completeness only when the ketone is present in excess of molar quantities as compared with the aluminum chloride. Two moles of acetophenone per mole of aluminum chloride gave the highest yields (73%). Quantities of aluminum chloride in excess of 1 mole per mole of acetophenone were essentially without effect in bringing about the reaction. Any excess of simple ketone beyond 2 moles tended to produce high molecular weight, viscous gums, and to reduce markedly the yield of dypnone. At low temperatures the condensation proceeds quite slowly and the formation of the gummy residues which are always present in small quantities when the reaction takes place at room temperature is strongly inhibited. At 40–50° the time for the reaction is shortened and the residue is markedly increased. Stirring has little effect.

Although hydrogen chloride is evolved continually during any period of heating of acetophenone and aluminum chloride, the simple explanation that the condensation is promoted by hydrogen halide is not tenable. This general type of condensation may be promoted by hydrogen halides,[3] it is true, but also by alkalies,[4] heat,[5] radiation,[6] zinc alkyls,[7] organoaluminum halides,[8] acetic anhydride,[9] sulfuric acid,[9] sodium pyrosulfate,[10] sodamide,[11] and aluminum and alkyl halides.[12]

The fact that the three valences of aluminum in aluminum chloride are occupied by chlorine atoms seemed incidental to the process of condensation. Therefore, a substance such as triphenylaluminum, in which the three valences are occupied by non-haloid groups, should bring about this condensation.[13] It was found that triphenylaluminum did condense acetophenone to yield dypnone although a portion of the organometallic compound reacted with the car-

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[1] This work was initiated while one of us was a faculty member at Tuskegee Institute.

[2] Calloway, *Chem. Rev.*, **17**, 327 (1935).

[3] Cologne, *Bull. soc. chim.*, [4] **49**, 426 (1931); Grignard and Cologne, *Bul. soc. chim. Romania*, **15**, 5 (1933); [*C. A.*, **28**, 101 (1934)].

[4] Kohler, "Organic Syntheses," Coll. Vol. I, 1932, p. 71.

[5] Mitchell and Reid, THIS JOURNAL, **53**, 336 (1931).

[6] Clark and Pickett, *ibid.*, **52**, 468 (1930).

[7] Delacre, *Bull. acad. roy. belg.*, [3] **22**, 470 (1892); [*Brit. Chem. Abstracts*, **62**, 993 (1892)].

[8] Leone and Braicovic, *Gazz. chim. ital.*, **55**, 301 (1925); [*C. A.* **19**, 2929 (1925)].

[9] Claisen and Claparède, *Ber.*, **14**, 2464 (1881).

[10] Odell and Hines, THIS JOURNAL, **35**, 83 (1913).

[11] Haller and Bauer, *Ann. chim.*, [8] **28**, 409, 413 (1913).

[12] Konowalow and Finogejew, *J. Russ. Phys.-Chem. Soc.*, **34**, 945 (1902); [*Brit. Chem. Abstracts*, [1] **84**, 264 (1903)].

[13] Gilman and Nelson, *Rec. trav. chim.*, **55**, 522, 527 (1936).

bonyl group. No methyldiphenylcarbinol was observed. There was isolated, however, a substance which gave every indication of being *as*-diphenylethylene. There was a residue of resinous material that undoubtedly resulted from further condensation of the β-unsaturated ketone.

$$C_6H_5COCH_3 \xrightarrow{(C_6H_5)_3Al} (C_6H_5)_2C(OH)CH_3 \xrightarrow{-H_2O} (C_6H_5)_2C{=}CH_2$$

From the general effectiveness of aluminum alcoholates as condensing agents, it may be that in both the case of aluminum chloride and of triphenylaluminum there was an intermediate formation of substances of the general type of R–O–Al–R_2 which actually promoted the condensation. Thus in the case of aluminum chloride, the aluminum salt may have been formed from the enol of acetophenone. From triphenylaluminum the salt may arise either by reaction with enolic acetophenone or more likely directly by reaction of triphenylaluminum with the acetophenone.

When benzaldehyde was substituted for one mole of the acetophenone and condensation was brought about by aluminum chloride, chalcone was isolated in excellent yields (91%). It is noteworthy here that the reaction proceeded more rapidly than when dypnone was formed.

Experimental Part

Dypnone from Ketone Synthesis.—To 13.3 g. (0.1 mole) of anhydrous aluminum chloride in 100 cc. of dry carbon disulfide in a 500-cc. three-necked balloon flask equipped with a mercury-sealed mechanical stirrer, a dropping funnel, and a reflux condenser closed by a tube of calcium chloride leading to a suitable trap, there was added dropwise 7.8 g. (0.1 mole) of redistilled acetyl chloride taking care that the temperature did not rise above 25°. After the resulting oily complex had stirred for fifteen minutes, there was added dropwise 7.8 g. (0.1 mole) of dry, thiophene-free benzene over a period of twenty minutes. The reaction was stirred for one hour, after which it was refluxed and stirred for twelve hours. Hydrogen chloride was evolved during this entire period, rapidly at first and more slowly toward the end of the reaction.

The dark brown, viscous reaction mixture was poured over 200 g. of crushed ice. The aqueous layer was separated and extracted with two 25-cc. portions of carbon disulfide. The washings were combined with the original carbon disulfide layer and washed with two portions of water and one of 10% sodium bicarbonate. After drying over sodium sulfate the solvent was removed on a water-bath.

Vacuum fractionation yielded 8.4 g. (70%) acetophenone, b. p. 106–109° (38–40 mm.), and 3 g. of dypnone, b. p. 160–165° (1 mm.). There was a gummy viscous residue of 1 g.

The dypnone was identified by the semicarbazone which melted at 150–151° and showed no depression when mixed with a sample of known material.[14]

In a duplicate run which was heated for only three hours, 10.1 g. of acetophenone was obtained (83%). There was no dypnone or residue.

Condensation of Acetophenone to Dypnone.—For all reactions involving stirring or refluxing the set-up described for the acylation above was used. Heat was applied to the appropriate reactants by means of a water-bath on a hot-plate. For all reactions not involving stirring or refluxing, the following set-up was used. A suitably sized Erlenmeyer flask was equipped with a rubber stopper fitted with a large straight calcium chloride tube completely filled with coarse calcium chloride.

In all cases the acetophenone was added slowly to the aluminum chloride in carbon disulfide. During this addition considerable heat was evolved. Reflux of the solvent was avoided by cooling with running water; 100 cc. of carbon disulfide was used for each tenth mole of aluminum chloride. *In every case hydrogen chloride was evolved throughout the reaction period.*

The products were isolated by the procedure given for the isolation of dypnone from the ketone synthesis above. Systematic variation of conditions showed that the best yields of dypnone were obtained when two moles of acetophenone were added to one mole of aluminum chloride at room temperature and allowed to stand for seven days, yield 73%.

The Synthesis of Chalcone.—Using essentially the same procedure as that outlined for dypnone chalcone was prepared by adding 12.1 g. (0.1 mole) of acetophenone to 13.3 g. (0.1 mole) of aluminum chloride in 100 cc. of carbon disulfide keeping the reaction cooled with tap water. After the resulting complex was formed, the reaction mixture was allowed to stand for thirty minutes with occasional shaking. There was then added slowly 10.6 g. (0.1 mole) of purified benzaldehyde. The flask was closed with a tube of calcium chloride and shaken occasionally during the first hour. It was then allowed to stand for four days. At the end of this time the liquid complex had solidified to definite yellow to brown crystals. The carbon disulfide was decanted and discarded. The crystals were washed with two portions of benzene and allowed to drain free of solvent by inverting the flask. Water was now added and the crystalline mass broken up with a stirring rod. When hydrolysis was complete the product was cooled in ice. The resulting yellow crystalline product was filtered off. After one crystallization from alcohol it melted at 54–56°, yield 19 g., 91% of theoretical. The m. p. of a sample mixed with an authentic specimen[4] was 55–56°.

Hydrolysis of the entire reaction mixture without decanting the carbon disulfide, as for dypnone, gave essentially the same results as obtained in the preceding chalcone run, when the product was distilled.

Reaction of Triphenylaluminum with Acetophenone.—Triphenylaluminum[15] was prepared in toluene solution from diphenylmercury[16] under nitrogen free from carbon dioxide, oxygen and moisture. To 190 cc. of a filtered solu-

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[14] Wilson and Macaulay, *J. Chem. Soc.*, **125**, 841 (1924).

[15] Gilman and Marple, *Rec. trav. chim.*, **55**, 133 (1936).

[16] Nesmeyanow, *Ber.*, **62**, 1012 (1929); Nesmeyanow and Kahn, *ibid.*, **62**, 1018 (1929).

tion of 7.7 g. (0.03 mole) of triphenylaluminum in a three-necked flask fitted with an inlet for nitrogen, a mechanical stirrer and a reflux condenser closed by a tube filled sufficiently with sulfuric acid to assure a positive nitrogen pressure, there was added 12 g. (0.1 mole) of acetophenone. No immediate reaction was perceptible. After thirty minutes a flocculent precipitate appeared. The mixture was now heated in an oil-bath at 100–115° for six hours after which it was allowed to stand for six hours at room temperature. The thick, pasty reaction mixture was poured into 100 cc. of water containing 2% nitric acid. The toluene layer was separated, washed with water and 10% sodium bicarbonate and dried over sodium sulfate. The solvent was removed by distillation and the residue was twice vacuum fractionated at 9 mm. Two fractions were obtained: (A) b. p. 108–120°, 3 g.; (B) b. p. 190–195°, 4 g.; residue, 3 g. that did not distill up to 270°. This residue set to a hard amber colored resin-like mass soluble in acetone but sparingly soluble in alcohol and ether.

Fraction B.—Dypnone by m. p. and mixed m. p. of oxime,[17] 133–134°.

Fraction A.—This material was shaken for fifteen hours with a saturated solution of sodium bisulfite to remove any ketone. The oil was then extracted with ether and dried over sodium sulfate. Distillation gave 2 g. of a product boiling at 272–277°; n^{14}D 1.6070; 0.1 g. of this material in dry chloroform immediately discharged the color of bromine[18] to form an addition product that evolved hydrogen bromide when the solvent was removed.

Oxidation[18] of 0.8 g. of this oil at 80° for five hours gave a product which when extracted from alkaline solution by ether would not crystallize at room temperature, but gave 1 g. of an oxime, melting[18] (p. 150) at 140–141° and showing no depression of m. p. when mixed with a known sample of benzophenone oxime. It was concluded that the substance was α,α-diphenylethylene.

In a run in which acetophenone was refluxed with sodium-dried toluene for thirty-six hours, no dypnone was found.

The authors are grateful to Mr. Thomas Campbell who kindly prepared some of the starting materials.

Summary

1. The evolution of hydrogen halide in the Friedel–Crafts ketone synthesis is not a satisfactory criterion for judging the optimum period of reaction.

2. Drastic and prolonged reaction conditions and especially the use of an insufficient proportion of aluminum chloride tend to encourage condensation of ketones primarily formed by acylation.

3. Aluminum chloride is capable of condensing acetophenone to form dypnone and a mixture of acetophenone and benzaldehyde to form chalcone.

4. Triphenylaluminum similarly will produce dypnone from acetophenone.

NASHVILLE, TENN. RECEIVED JANUARY 18, 193

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[17] Henrich and Wirth, *Ber.*, **37**, 731 (1904).

[18] Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, Inc., N. Y., Vol. I, First Edition, 1904, p. 194.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Oxidation of Ethyl Mercaptan and Ethyl Disulfide by Bromine in the Presence of Water

BY H. A. YOUNG

Dilute carbon tetrachloride solutions of ethyl mercaptan and ethyl disulfide are oxidized in a normal manner[1] to ethyl sulfonic acid by bromine water, as represented by the equations

$$RSH + 3Br_2 + 3H_2O = C_2H_5SO_3H + 6HBr \quad (1)$$

$$C_2H_5SSC_2H_5 + 5Br_2 + 6H_2O = 2C_2H_5SO_3H + 10HBr \quad (2)$$

Ethyl mercaptan is converted instantaneously and quantitatively to the disulfide in the absence of water, in accord with the results of Otto and Rossing.[2]

Experimental Part

Equivalents of Bromine Used per Mole of Sulfur Compound

Ethyl Mercaptan.—Carbon tetrachloride solutions of the mercaptan were prepared and analyzed just before use by the iodimetric method of Reid.[3] A measured volume of mercaptan solution (approximately 0.005 *M*) was introduced into a 250-cc. glass-stoppered flask containing 100 cc. of water and a measured volume of a known solution of bromine (excess) in carbon tetrachloride was added immediately. The flasks were then put in a shaker in a 25° thermostat, and after various times were withdrawn, 2 g. of solid potassium iodide added, and the liberated iodine was titrated with 0.1 *N* sodium thiosulfate solution. The results of a series of such experiments showed that 6.00 ± 0.03 equivalents of bromine were used per equivalent of

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[1] It is well known that strong oxidizing agents convert mercaptans and disulfides to the corresponding sulfonic acids. Friedman [*Beitr. Chem. Physiol. Path.*, **3**, 25, 38 (1903)] has shown that bromine oxidizes cystine and cysteine to cysteic acid.

[2] Otto and Rossing, *Ber.*, **19**, 3136 (1886).

[3] Sampey and Reid, THIS JOURNAL, **54**, 3405 (1932).

mercaptan and that the reaction was complete in about twenty-four hours.

Ethyl Disulfide.—Since no method of analysis is known for disulfides, it was necessary to weigh a sample of ethyl disulfide for each experiment. This was done by introducing the disulfide from a dropping pipet with a long capillary into a weighed, thin-walled glass weighing ampoule. The ampoule was iced, sealed, dried and reweighed, after which it was dropped into a 250-cc. glass-stoppered flask containing a known excess amount of bromine in carbon tetrachloride and 100 cc. of water. The subsequent treatment was the same as with the mercaptan.

In these experiments it was found that the bromine used was almost always about 1% high. Blank experiments showed that this error was due to loss of bromine during the manipulations, probably chiefly during the introduction of the ampoule containing the ethyl disulfide. Table I gives two typical experiments.

TABLE I

Expt.	R_2S_2, g.	Eq. Br_2 per mole R_2S_2	Correction	Eq. Br_2 per mole R_2S_2 corr.
1	0.0776	10.11	0.15	9.96
2	.1324	10.14	.14	10.00

In view of the above data it seems safe to conclude that these measurements are good to about 1.5% in spite of the relatively high volatility of every substance involved, and that the main reactions are probably those suggested in equations 1 and 2.

Oxidation of Ethyl Mercaptan by Dry Bromine.—The amount of bromine used by ethyl mercaptan in the absence of water was measured by mixing dilute carbon tetrachloride solutions of a known amount of ethyl mercaptan with a known excessive amount of bromine. After various times, the solutions were shaken with aqueous solutions of potassium iodide and the resulting iodine titrated with sodium thiosulfate solution.

The amount of hydrogen ion produced in the reaction was measured in a similar fashion by using excess ethyl mercaptan. The carbon tetrachloride solutions were extracted and washed with water and the extract titrated with standard sodium hydroxide solution.

The results of a series of experiments in which the mercaptan concentration varied from 0.003 to 0.03 *M* showed that 1.00 ± 0.01 equivalents of bromine were used per mole of mercaptan; those of a second series in which the bromine concentration varied from 0.003 to 0.025 *M* indicated that 1.00 ± 0.03 moles of hydrogen ion were liberated per equivalent of bromine used.

These experiments also showed that the reaction was complete within forty-five seconds after mixing, and that no further reaction took place.

Identification of Ethyl Sulfonic Acid.—The oxidation reactions were allowed to go to completion in reaction mixtures containing 12 g. of the sulfur compound and 100 g. of bromine. The water layer was separated, concentrated by evaporation, neutralized with sodium hydroxide and evaporated to dryness. After drying at 120° for three hours, the sodium ethyl sulfonate was extracted by use of hot 95% ethyl alcohol. The sodium salt was then converted to the corresponding acid chloride by the method of Marvel, Helfrick and Belsley.[4] The acid chlorides obtained boiled at 177° which compares with a boiling point of 177.5° given by Carius.[5]

Summary

1. Ethyl mercaptan and ethyl disulfide are oxidized to ethylsulfonic acid by bromine water, the oxidation requiring 3 and 5 moles of bromine per mole of the sulfur compound, respectively.

2. Ethyl mercaptan is very rapidly oxidized to ethyl disulfide by dry bromine.

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(4) Marvel, Helfrick, and Belsley, THIS JOURNAL, **51**, 1272 (1929).

(5) Carius, *J. prakt. Chem.*, [2] **2**, 264 (1870).

DAVIS, CALIF. RECEIVED DECEMBER 11, 1936

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Rate of Oxidation of Ethyl Disulfide by Bromine

BY H. A. YOUNG AND M. B. YOUNG

In the preceding paper,[1] it has been shown that bromine oxidizes ethyl disulfide to ethylsulfonic acid in the presence of water, and that under proper conditions five moles of bromine are used for each mole of disulfide oxidized. While performing the experiments described in the above paper, it was noted that immediately upon the addition of ethyl disulfide to a carbon tetrachloride solution of bromine, the color of the latter changed perceptibly, becoming lighter and a more pronounced yellow. Also when excess disulfide was added to bromine, distributed between water and carbon tetrachloride, the bromine was almost completely removed from the water layer.[2] These observations suggest the rapid formation of an addition compound between bromine and ethyl disulfide. That the formation of the addition compound is reversible is shown by the fact that a known amount of bromine which has been treated for several hours

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(1) H. A. Young, THIS JOURNAL, **59**, 811 (1937).

(2) A similar effect is noticed with iodine. Excess ethyl disulfide in carbon tetrachloride will remove enough iodine from a water layer to prevent the formation of a blue color in the presence of starch, as first noted by Sampey and Reid, *ibid.*, **54**, 3405 (1932).

with ethyl disulfide in carbon tetrachloride solution (water absent) shows no loss in oxidizing power. The purpose of the present work is to investigate the addition compound by measuring the rate of disappearance of bromine during the oxidation of ethyl disulfide in the two-phase system consisting of bromine and disulfide dissolved in carbon tetrachloride as one phase and bromine in water as the second. Since the final products of the reaction are found in the water layer, the reaction steps involving water presumably take place either across the boundary of the carbon tetrachloride or in the carbon tetrachloride itself with subsequent diffusion. The authors undertook the investigation realizing the difficulties involved in the interpretation of rate measurements in such a heterogeneous system, as pointed out by Bell,[3] yet they believe the simplicity of the obtained initial rates is significant.

Experimental Part

The desired amount of ethyl disulfide for each experiment was weighed in a weighing ampoule, and the ampoule was broken in 100 cc. of carbon tetrachloride which was at the reaction temperature and which was contained in a 300-cc. glass-stoppered flask. A bromine solution for each experiment was prepared and analyzed iodimetrically after being brought to the reaction temperature.

An experiment was carried out as follows: 100 cc. of water at 25° and 50 cc. of bromine solution were introduced, respectively, into a 300-cc. glass-stoppered conical flask. Fifteen cc. of the disulfide solution was pipetted into the flask and the mixture was then placed in a shaker in a thermostat at 25.0 ± 0.1°. Zero time was taken when half the disulfide had run into the flask. In each experiment five such mixtures were prepared. At various intervals, the flasks were removed from the thermostat, 2 g. of solid potassium iodide was added and the liberated iodine titrated with sodium thiosulfate solution.

Experimental Results

The bromine concentrations for the carbon tetrachloride layer were calculated on the assumption that all of the bromine was in the carbon tetrachloride. This point will be referred to later. These bromine concentrations were plotted as abscissas against time in minutes as ordinates, and values of $-d(Br_2)/dt$ obtained by taking slopes of the tangents. After preliminary work indicated that the values of $-dBr_2/dt$ taken at zero time were reproducible to within 5% a series of fourteen experiments was made. There were occasional inexplicable erratic points which obviously lay off the bromine–time curves.

TABLE I

REPRESENTATIVE EXPERIMENTAL DATA

	Expt. 1 R_2S_2 = 0.0133		Expt. 2 R_2S_2 = 0.00542		Expt. 5 R_2S_2 = 0.0252	
	Concentrations					
Time, min.	Br_2	Corr. Br_2	Br_2	Corr. Br_2	Time, min.	Br_2 concn.
0	0.0785	0.0739	0.0775	0.0730	0	0.0158
60	.0642	.0598	.0713	.0670	20	.0123
120	.0533	.0492	.0670	.0627	52	.00870
180	.0467	.0427	.0632	.0588	80	.00788
240	.0411	.0374	.0611	.0568	110	.00586
300	.0371	.0336	.0597	.0555	155	.00453

In only one experiment was there more than one such point, and in that case the experiment was discarded. Table I contains the complete data for three representative experiments; Fig. 1 is the bromine–time plot for the same experiments.

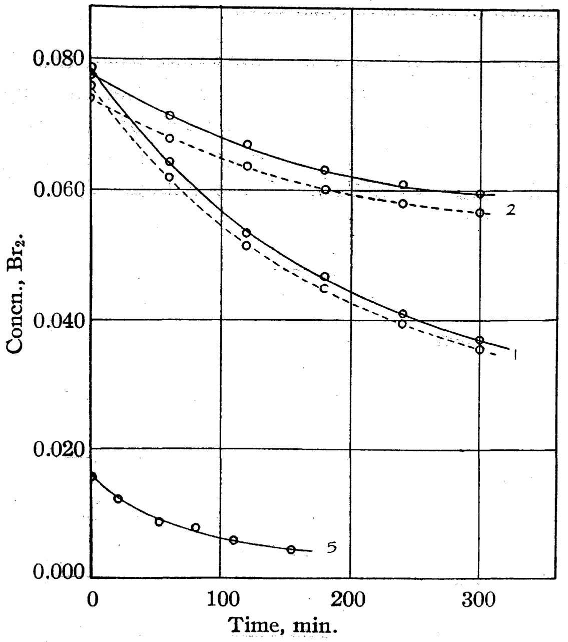

Fig. 1.—Plot of bromine concentration against time in minutes for Expts. 1, 2 and 5.

Table II contains a summary of the thirteen experiments. The initial concentrations of the reactants are given in columns two and three and the initial values of $-dBr_2/dt$ in column 4.

Discussion of Results

From the initial slopes in Expts. 1, 2 and 3, it is seen that when the concentration of bromine is high and that of disulfide low, the initial rate is independent of bromine concentration and may be expressed by the equation $-dBr_2/dt = k_1 (R_2S_2)$. The values given in column 5 of Table II indicate that k_1 has an average value of 0.020. Examination of the initial rates obtained in

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(3) Bell, *J. Phys. Chem.*, **32**, 882 (1928).

TABLE II

SUMMARY OF EXPERIMENTS

Expt.	R_2S_2, initial	Br_2, initial	$-\frac{d(Br_2)}{dt}$ initial	$-\frac{d(Br_2)}{dt}\Big/R_2S_2$	$-\frac{d(Br_2)}{dt}\Big/R_2S_2$ corr.	$-\frac{d(Br_2)}{dt}\Big/Br_2$	$R_2S_2(Br_2)_2$
1	0.0133	0.0785	0.000259	0.019	0.019		0.0133
2	.00542	.0775	.000115	.021	.020		.00542
3	.00493	.0328	.000101	.020	.020		.00493
4	.0302	.0188	.000213			0.011	.00940
5	.0252	.0158	.000180			.011	.00790
6	.0548	.0187	.000201			.011	.00935
7	.0526	.0416	.000415			.010	.0208
8	.0275	.0437	.000500			.011	.0218
9	.0279	.0507	.000523			.010	.0253
10	.0245	.0402	.000490			.012	.0201
11	.0254	.0401	.000514			.013	.0200
12[a]	.0272	.0182	.000464			.025	
13[b]	.0154	.0854	.000279	.018			

[a] Expt. 12, original $H^+ = 0.10\ M$. [b] Expt. 13, shaker reduced to one-fourth usual speed.

Expts. 4, 5, 6 and 7 indicates that when the disulfide concentration is high and the bromine low, the initial rate is independent of the disulfide concentration, and may be expressed by $-dBr_2/dt = k_2(Br_2)$. From column 7, Table II, k_2 has an average value of 0.011.

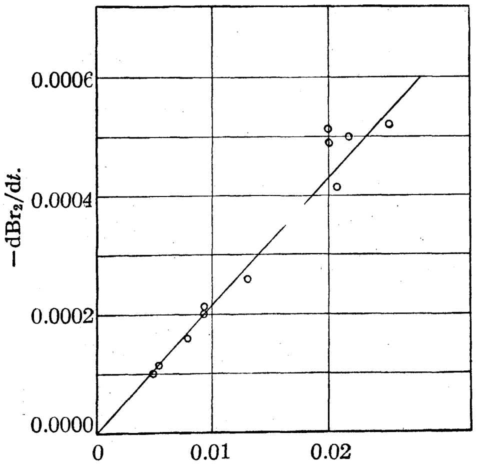

Fig. 2.—Initial rates of disappearance of bromine plotted against calculated concentration of intermediate.

The simplest explanation for the results of Expts. 1 to 7 is that the initial rate of using bromine is proportional to the concentration of a compound which is in equilibrium with one molecule of disulfide and two molecules of bromine, as represented by the equation

$$R_2S_2 + 2Br_2 \rightleftarrows R_2S_2(Br_2)_2$$

From the results of Expts. 8, 9, 10, 11 as shown in column 7 of Table II, it appears that within the limits of experimental error the formation of the addition compound is complete.

The original assumption that all the bromine is found in the carbon tetrachloride may now be seen to produce no appreciable error in the experiments in which the disulfide is in excess, for in this case all but the minute equilibrium quantity of the bromine is in the form of addition compound which is insoluble in water. With bromine in excess, however, an appreciable amount of it is in the water layer. Using 27 as the distribution ratio of bromine between carbon tetrachloride and water and assuming the concentration of the intermediate to be that of the disulfide, corrected values of bromine concentrations in the carbon tetrachloride layer were obtained and plotted against time as before for Expts. 1, 2 and 3. The corrected data for Expts. 1 and 2 are given in Table I, and the corrected plots are shown by broken curves in Fig. 1. In only Expt. 2, where the value of k_1 dropped from 0.021 to 0.020, was the corrected initial value of k_1 significantly different from the uncorrected value.

Concentrations of the addition compound, taken as one-half the bromine concentration when the disulfide is in excess and as the disulfide concentration when the bromine is in excess are listed in column 8 of Table II. These concentrations are plotted against the corresponding initial values of $-d(Br_2)/dt$ in Fig. 2. The points lie very close to a straight line of slope 0.021, so that within the limits of experimental error the initial rates are given by the expression $-d(Br_2)/dt = 0.021[R_2S_2(Br_2)_2]$. The two points which lie farthest from the line represent Expts. 10 and 11, in which the uncertainties in the slopes are probably greater than in any other of the experiments.

The rate measurements do not distinguish between intermediates of the types $R_2S_2(Br_2)_2$ and $RSBr_2$, although the existing independent evidence appears to favor the breaking of the sulfur–sulfur linkage by bromine. Zincke and Farr[4] have prepared mono-*o*-nitrophenyl sulfur bromide from the corresponding disulfide by treatment with bromine. Hunter and Sorenson[5] in their discussion of the mechanism of the reduction of sulfonyl bromides by phosphorus tribromide assumed an equilibrium of

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[4] Zincke and Farr, *Ann.*, **391**, 67 (1912).

[5] Hunter and Sorenson, THIS JOURNAL, **54**, 3668 (1932).

the form $RSSR + Br_2 \rightleftarrows 2RSBr$. They were able to demonstrate that *o*-nitrophenyl sulfur bromide gave small amounts of *o*-nitrophenyl disulfide upon standing, but were unable to prepare the sulfur bromide from the disulfide and bromine. Zincke and Frohneburg[6] have studied the oxidation of dithiohydroquinone and thiocresol by chlorine and bromine in the presence of water and have postulated the first step to be the formation of a disulfide, followed by an intermediate of the type $RSBr_3$.

It seems probable, therefore, that the oxidation of ethyl disulfide by bromine in the presence of water takes place in steps, the first of which is a rapid reversible one of the type $2Br_2 + RSSR \rightleftarrows 2RSBr_2$. The second and rate determining step is probably the hydrolysis of the product of the first reaction, *i. e.*, $RSBr_2 + H_2O = RSO + 2HBr$. In view of the recent work of Johnson and Sprague[7] who isolated ethyl sulfonyl bromide from aqueous solutions when S-ethylisothiourea hydrogen bromide was oxidized by bromine at temperatures below 5°, and the work of Zincke and Frohneburg,[6] who showed that the ultimate oxidation product of both dithiohydroquinone and thiocresol by bromine in the presence of water was a sulfonyl bromide, it seems probable that another of the intermediate products in the system under consideration is ethyl sulfonyl bromide.

Effect of Hydrogen Ion and Rate of Shaking

The presence of hydrogen ion materially increases the initial rate as is indicated by Expt. 12. In this experiment the initial hydrogen ion concentration was 0.10 *N* and the value of k_2 obtained was 0.025 as contrasted with 0.011, the average value in the other experiments. The accelerating effect of hydrogen ion was not unexpected in view of the results of some measurements on the rate of oxidation of ethyl mercaptan by excess bromine in the presence of water. As shown in the preceding paper, the first step in the oxidation of the mercaptan is the rapid formation of ethyl disulfide with the liberation of hydrobromic acid, so that except for the presence of hydrogen ion the mercaptan experiments would be identical with those involving disulfide. The initial rates in the mercaptan experiments were found to be determined by the mercaptan concentrations, but were anomalously high. The effect of hydrogen ion upon the initial rate is being investigated further.

The effect of the rate of shaking upon the reaction rate is shown by Expt. 13 in which the speed of the shaker was reduced to one-fourth its usual value. The initial rate yielded a value of k_1 equal to 0.018, which is not far from the average value of 0.020. However, in the latter stages of this experiment the reaction rate was much slower than usual. This suggests that toward the end of the reaction the rate determining step is one of diffusion. If such is the case, the rate of using bromine in all of the experiments except number 13 might finally approach the same first order rate law. To test this hypothesis, values of $-dBr_2/dt$ at various times were plotted against calculated concentrations of the intermediate $[R_2S_2(Br_2)_2]$ (Fig. 3). The curves in that plot appear to approach a straight line of slope 0.014.

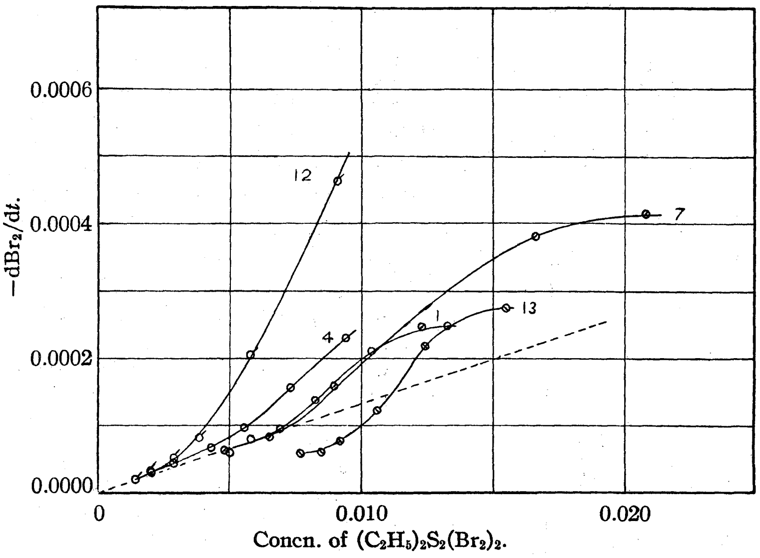

Fig. 3.—Rates of disappearance of bromine plotted against calculated concentration of intermediate.

Summary

1. The rate of the reaction between carbon tetrachloride solutions of bromine and ethyl disulfide in the presence of water has been measured at 25°.

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[6] Zincke and Frohneburg, *Ber.*, **42**, 2721 (1909); **43**, 1348 (1916).

[7] Johnson and Sprague, THIS JOURNAL, **58**, 1348 (1936).

2. The initial rates have been shown to be represented by the equation $-dBr_2/dt = k \times [R_2S_2(Br_2)_2]$ where k is a function of the rate of shaking.

3. The first steps in the oxidation of ethyl disulfide by bromine in the presence of water are suggested as

$$R_2S_2 + 2Br_2 \rightleftarrows 2RSBr_2, \text{ and} \qquad (1)$$

$$RSBr_2 + H_2O = RSO + 2H^+ + 2Br^- \qquad (2)$$

DAVIS, CALIF. RECEIVED DECEMBER 11, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WHEATON COLLEGE]

Raman Spectra. II. Monomethoxy Derivatives of Ethyl Benzoate

BY DOROTHY D. THOMPSON

The Raman spectra of several derivatives of benzoyl chloride were determined[1] in an attempt to find a relationship between this property and the rates of esterification of the acid chlorides, and these spectra were compared with those of the corresponding ethyl esters.[2] Since, however, the spectra of the methoxy derivatives of ethyl benzoate had not been determined, it was thought advisable to prepare them and study their Raman spectra.

Experimental

Apparatus.—The same Hilger E-439 glass spectrograph,[3] system of filters, light source, Raman tube and photograph plates were employed as were described in a previous paper.[1] The frequencies of the lines were determined as before except that the deviation curves were made from the difference from linear dispersion in terms of wave numbers instead of wave lengths. The accuracy is about the same as before (±1 for the strong, sharp lines, but a greater error up to ±4 cm.$^{-1}$ for very weak diffuse lines).

Purification of Compounds.—The esters were prepared from the corresponding acid chloride and absolute alcohol or by the action of absolute alcohol saturated with hydrogen chloride on the corresponding acid (*o*-methoxybenzoic acid prepared by methylation of salicylic acid with dimethyl sulfate; *p*-methoxybenzoic acid was Eastman White Label). The esters were washed rapidly with ice-cold sodium carbonate and several times with cold water, then dried over calcium chloride. They were distilled *in vacuo* from an ordinary Claisen flask several times or until the index of refraction of the major portion remained constant. One distillation through a modified Vigreux[4] column showed that the boiling point range was in every case not greater than 0.2°. The densities were determined in the usual way with a pycnometer having a capacity of 5 ml. The average deviations of three to five independent determinations never exceeded one part in twenty thousand. The calculations were made in the usual way correcting for the buoyancy of air and for the expansion of glass. The indices of refraction were measured with an Abbé refractometer and the molecular refractions calculated from the equation of Lorenz and Lorentz.

Data

Explanation of Tables.—The values of the Raman spectra have been summarized in the usual way. The value for the Raman shift is followed by a number in parentheses indicating the relative intensity (estimated)—the large numbers indicating greater intensity, the letter "b" for broad and "d" for diffuse. This is followed by letters indicating the mercury exciting lines as follows: a = 24,705 cm.$^{-1}$, b = 24,516 cm.$^{-1}$, c = 23,039 cm.$^{-1}$, d = 22,995 cm.$^{-1}$ and e = 22,938 cm.$^{-1}$. Each compound was photographed four times—twice with "Greenish Nultra" filter only, with long and short exposure times, once with "Greenish Nultra" + quinine sulfate, and once with "Red-Purple Ultra" glass + sodium nitrite. Each Raman line occurred on at least two plates unless indicated with a *.

Ethyl *o*-Methoxybenzoate.—Boiling point 104.4–104.5° at 2 mm.; n^{20}_D 1.5224; d^{20}_4 1.1124; d^{25}_4 1.1077; R_M calcd. 48.40, obsd. 49.42.

$\Delta\nu$ = 80(0)(a, +b, c, e); 115(00)(a, e); 230(00)(a, e); 276(0)(a, e); 305(00)(a, e); 333(4)(a, b, c, e); 395(00)(a, e); 434(0)(a, d, e); 459(00)(a, e); 523(0)(a, e); 563±5-(1b)(a, e); 582(2)(a, b, d, e); 657(2)(a, b, ±e); 780±10-(4band)(a, d, e); 854(2)(a, e); 877(1)(a, e); 1020(0b)(a, e); 1049(6)(a, b, c, e); 1166(4)(a, b, d, e); 1251(8b)(a, b, d, e); 1302(2d)(a, b, e); 1354(00)(a, e); 1448(0)(a, c, e); 1491(0)(a, e); 1600(6)(a, c, d, e); 1721(2d)(b, d, e); 2929(1)(a); 3077(2)(a).

Ethyl *m*-Methoxybenzoate.—Boiling point 97.6–97.8° at 1 mm.; n^{20}_D 1.5161; d^{20}_4 1.0993; d^{25}_4 1.0949; R_M, calcd. 48.40, obsd. 49.50.

$\Delta\nu$ = 94(00)(a, +b); 107(00)(a); 128(00)(a, e); 192(0)(e); 223(00)(a, e); 252(00)(a, e); 263(0)(e); 301(0)(a, e); 330(2)(a, e); 390(00)(a, e); 416(00)(a, e); 452(2)(a, b, e); 482(0)(e); 550(00)(a, e); 572(2d)(a, e); 588(0)(a); 667(3)(a, e); 765(2)(a, e); 804(2b)(a, e); 863(2d)(a, e); 996(10)(a, b, c, d, e); 1038(00)(a, e); 1102-(0b)(a, e); 1172(1)(a, b, e); 1235(00)(a, e); 1281(10b)(a,

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(1) Thompson and Norris, THIS JOURNAL, 58, 1953 (1936).

(2) Kohlrausch and Pongratz, *Monatsh.*, 63, 427 (1933–1934); Kohlrausch and Stockmair, *ibid.*, 66, 323 (1935).

(3) The author wishes to express appreciation to the Research Laboratory of Organic Chemistry of the Massachusetts Institute of Technology for the use of this apparatus and to the Physics Department for the use of their Hilger comparator.

(4) Thanks are due to Mount Holyoke College Chemical Laboratory for this column.

* Occurred on one plate only.

e); 1320(3)(a, e); 1366(1)(a, e); 1391(0)(a, e); 1430(00)(a, e); 1455(3d)(a, e); 1600(10b)(a, c, e); 1718 (9)(b, d, e); 2939(2)(a); 2978(00)(a); 3078(3)(a).

Ethyl *p*-Methoxybenzoate.—Boiling point, 104.2–104.4° at 2 mm.; $n^{20}{}_D$ 1.5254; $d^{20}{}_4$ 1.1038; $d^{25}{}_4$ 1.0994; R_M, calcd. 48.40, obsd. 50.05.

$\Delta\nu$ = 120(00)(a, e); 284(0)(a, b, d, e); 311*(0)(e); 326*(0)(e); 381*(0)(e); 437*(0)(e); 614(2)(a, c, e); 635(3)(a, b, e); 777(0b)(a, e); 801(2d)(a, e); 855(5)(a, b, d, e); 1012(0)(a, e); 1108(3)(a, e); 1169(10b)(a, b, c, d, e); 1216(0)(a); 1257(8)(a, b, d, e); 1277(7)(a, b, e); 1314(3b)(a, b, d, e); 1364(3b)(a, d, e); 1392(0)(a, e); 1420(1)(a, e); 1455(1 v. b.)(a, e); 1577(0)(a, e); 1607(10)(a, c, e); 1709(8b)(b, c, d, e); 2837(0b)(a); 2875(0)(a); 2933(3)(a); 2969(1b)(a); 3070(3b)(a).

Discussion

When the Raman spectra of these methoxy derivatives of ethyl benzoate are compared with the spectra of other esters which have substituents in corresponding positions, one striking difference appears. The number of weak lines of frequency difference of less than 600 cm.$^{-1}$ is much greater in each of these new spectra than in that of any other corresponding ester—even greater than in the spectrum of its acid chloride. Nor does this seem to be due to a shift toward lower frequencies of normally occurring higher frequencies since the correspondence of the rest of the spectra is almost perfect for all three position substitutions. The difference is probably not due to a difference in technique, for the comparison of the spectra of the acid chlorides determined by the author[1] shows no such disagreement with those of the same compounds determined by Kohlrausch, Pongratz and Stockmair.[5] Perhaps there is a relationship between this phenomenon and the optical exaltation to 1 ml. observed for ethyl *o*-methoxybenzoate of 2 ml. for the para derivative. Although no significant reason for this large number of low frequencies in the methoxy compounds can be advanced now, it was felt that the data should be published so that they will be available for interpretation when Raman spectra are better understood.

Summary

The Raman spectra of pure methoxy derivatives of ethyl benzoate have been determined and compared with the spectra of other derivatives of ethyl benzoate and of benzoyl chloride. The boiling points, densities, indices of refraction and molecular refractions for these compounds have, also, been determined and recorded.

[5] Kohlrausch, Pongratz and Stockmair, *Monatsh.*, **67**, 104 (1935–1936).

NORTON, MASS. RECEIVED FEBRUARY 8, 1937

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Infrared Absorption of Mixtures of Methyl Alcohol with Ethyl Formate and with Ethyl Acetate

BY DUDLEY WILLIAMS[1] AND WALTER GORDY[2]

Recently a series of experiments[3] has been made on the infrared absorption spectra of water, alcohol, and aniline in various solutions of other liquids. In every case when the solvent contained the strongly electronegative atoms, oxygen or nitrogen, having unshared electron pairs, pronounced changes were observed in the intensity and position of the vibrational OH band of alcohol and water, and in the NH band of aniline. In some cases certain changes were likewise observed in the spectrum of the solvent. For example, in mixtures of alcohol with acetone the vibrational band of the OH alcohol group was shifted to the shorter wave lengths, and its intensity was increased, while the CO band of acetone was shifted to the longer wave lengths and its intensity was increased correspondingly. It was suggested that these results indicate some type of interaction, possibly the formation of hydrogen bonds between the solute and solvent molecules. For the purpose of determining whether these results indicate some general type of interaction, the study has been continued, and in the present article results obtained from observations of the absorption spectra of different mixtures of methyl alcohol with ethyl formate and with ethyl acetate are discussed.

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[1] Now at the University of Florida.

[2] Now at Mary Hardin-Baylor College.

[3] (a) Walter Gordy, *J. Chem. Phys.*, **4**, 769 (1936); (b) *Phys. Rev.*, **50**, 1151 (1936); (c) THIS JOURNAL, **59**, 464 (1937).

Experimental

The apparatus and experimental method were the same as those used in the previous investigations[3] and will not be described here. The methyl alcohol and ethyl acetate were Baker "Certified Products." The ethyl formate was prepared by the action of formic acid on absolute ethyl alcohol, the ethyl formate being fractionated off during the reaction.

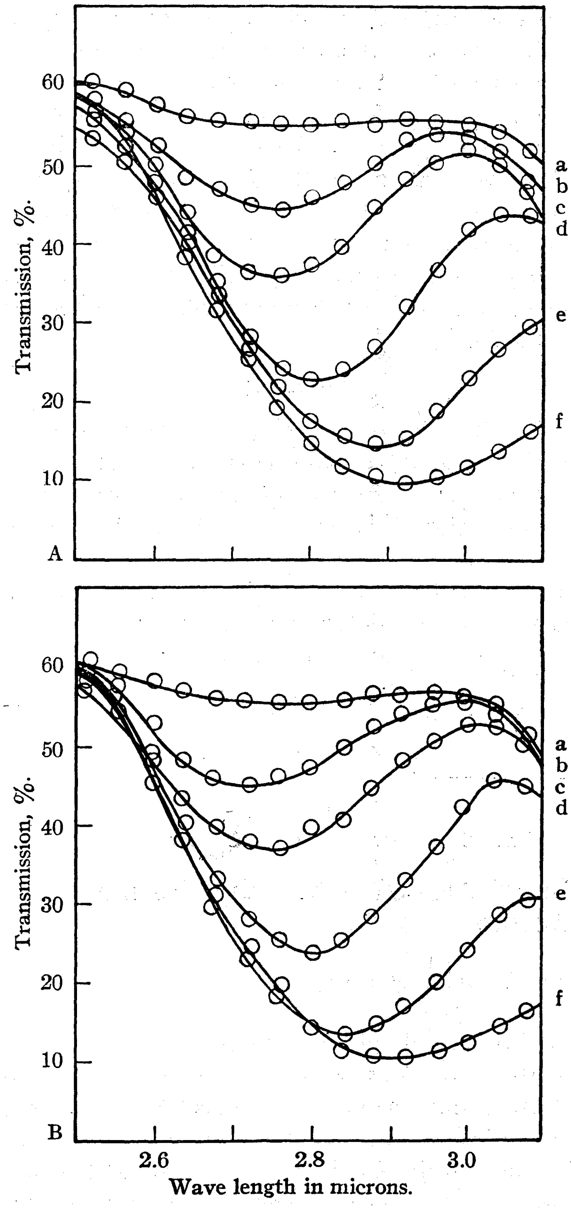

Fig. 1.—A. Transmission of methyl alcohol–ethyl formate mixtures: (a) pure ethyl formate; (b) 6.25% alcohol; (c) 12.5% alcohol; (d) 25% alcohol; (e) 50% alcohol; (f) pure alcohol. B.—Transmission of methyl alcohol–ethyl acetate mixtures: (a) pure ethyl acetate; (b) 6.25% alcohol; (c) 12.5% alcohol; (d) 25% alcohol; (e) 50% alcohol; (f) pure alcohol.

Results

The effects of ethyl acetate and of ethyl formate on the fundamental vibrational band of the OH alcohol group will be evident from Fig. 1. The center of the band in pure methyl alcohol appears at 2.9 μ. When the alcohol is mixed with either of the esters the band appears at shorter wave lengths, and the magnitude of the shift increases as the ester concentration in the mixture is increased. For alcohol concentrations as low as 12.5% in either ester the center of the band appears at about 2.74 μ. The intensity of the band does not decrease in proportion to the number of absorbers. This will be evident from a comparison of some of the experimental curves with theoretical ones for the same mixtures, computed on the assumption that neither component of the mixture influences in any way the spectrum of the other. In Fig. 2 the theoretical curves for mixtures of 12.5 and 6.25% methyl alcohol in ethyl acetate are shown with the experimental curves for the same mixtures. The method used in determining the theoretical transmission of a

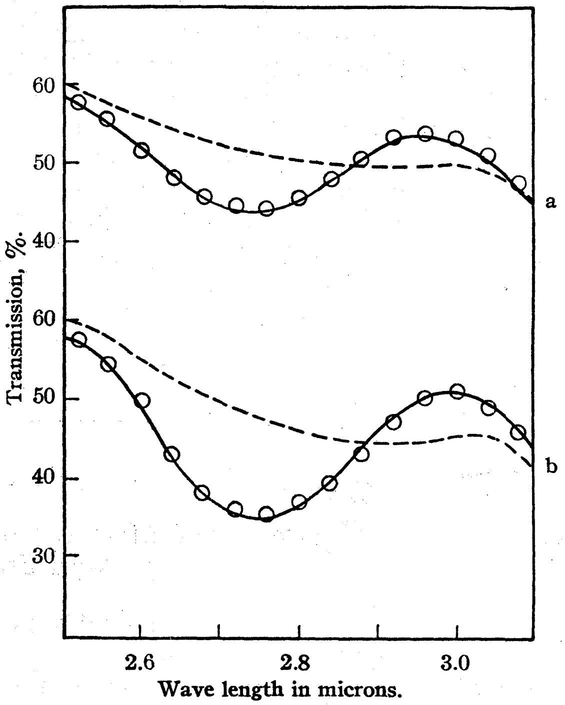

Fig. 2.—Comparison of theoretical with experimental transmission of some methyl alcohol–ethyl acetate mixtures: (a) 6.25% alcohol; (b) 12.5% alcohol.

mechanical mixture has been given in a previous paper[3c] and will not be repeated.

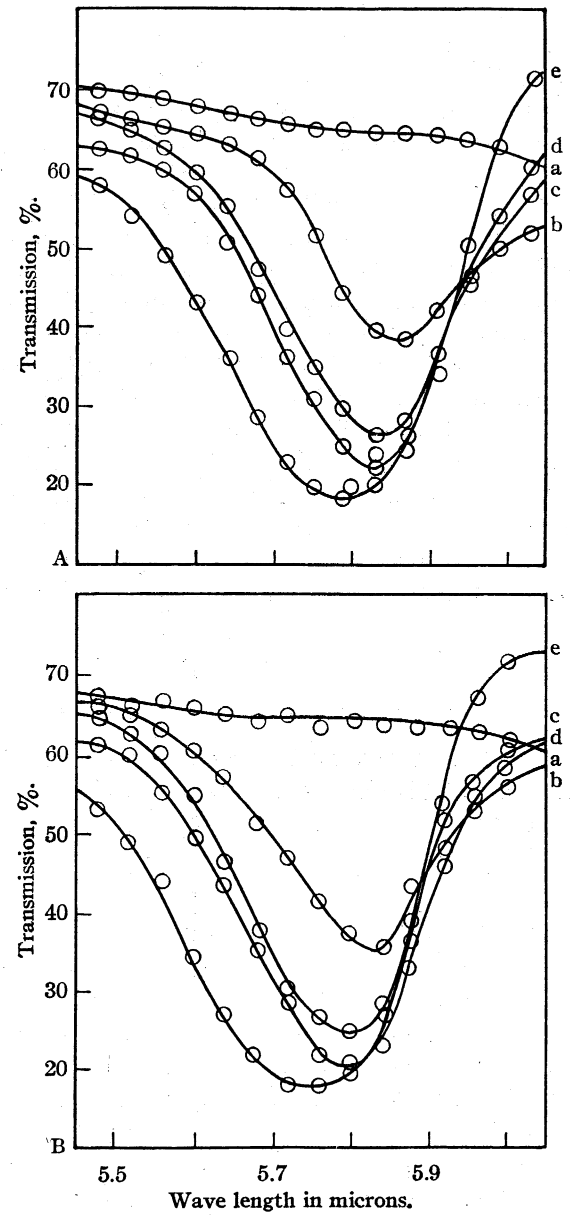

Fig. 3.—A. Transmission of methyl alcohol–ethyl formate: (a) pure alcohol; (b) 6.25% ethyl formate; (c) 12.5% ethyl formate; (d) 25% ethyl formate; (e) 50% ethyl formate; (f) pure ethyl formate. B.—Transmission of methyl alcohol–ethyl acetate mixtures: (a) pure alcohol; (b) 6.25% ethyl acetate; (c) 12.5% ethyl acetate; (d) 25% ethyl acetate; (e) 50% ethyl acetate; (f) pure ethyl acetate.

The vibrational band of the CO group in ethyl formate appears at about 5.79 μ, and in ethyl acetate it appears at about 5.75 μ. Figure 3 shows the effects of methyl alcohol on this band. In each of the esters the band is shifted to the longer wave lengths, and its intensity is increased by the methyl alcohol. The shift amounts to 0.08 μ for alcohol concentrations of 88.5%. Theoretical curves for two of the mixtures are given in Fig. 4. A study was also made of the effects of alcohol on the band appearing at about 8 μ in the two esters. No shifts in the position of the band could be detected. The curves for these mixtures are not shown. Due to the overlapping of bands of the two components it was not found practicable to study other bands appearing between 2.5 and 8.5 μ. The CO band of ethyl acetate was studied for various concentrations of ethyl acetate in isopropyl ether. The ether does not produce shifts and intensity changes in the band as does alcohol.

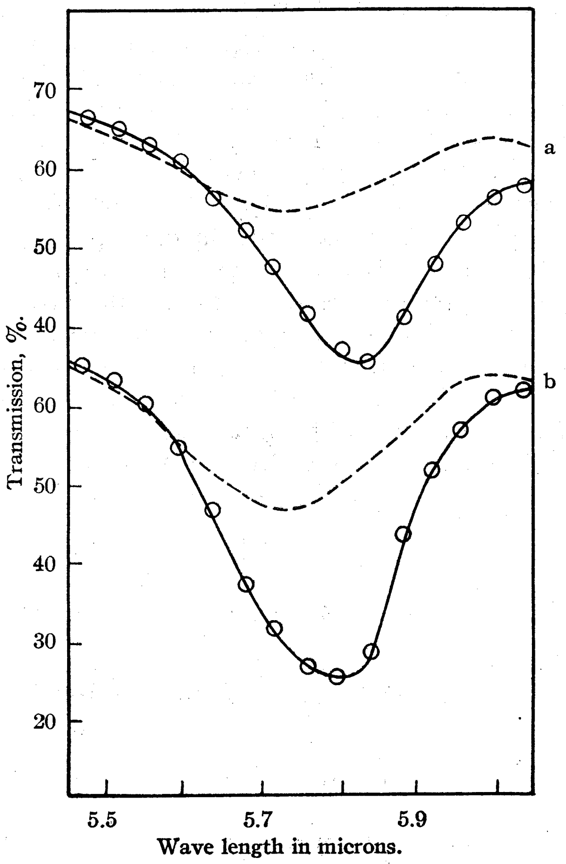

Fig. 4.—Comparison of theoretical with experimental transmission of some methyl alcohol–ethyl acetate mixtures: (a) 12.5% ethyl acetate; (b) 25% ethyl acetate.

Discussion

Since the discovery of the hydrogen bond[4] it has been generally believed that alcohols in

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[4] W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920).

the liquid state are associated through the formation of hydrogen bonds. The OH band appears at longer wave lengths and is much broader in the liquid than in the vapor state.[5] The changes in the character of this band as the alcohol passes from the vapor state to the liquid state are evidence that the OH group participates in the association process. Although in ethyl acetate and in ethyl formate the OH band is shifted to the shorter wave lengths, and this may indicate the breaking of hydrogen bonds between the alcohol molecules, the band does not become sharp, as it does for alcohol in the vapor state. It may be possible to interpret these results by assuming that as the ester content in the mixture is increased the polymerization of the alcohol is decreased and that the alcohol becomes associated to some degree with the ester through the formation of weak hydrogen bonds between the hydroxyl group of the alcohol and the carbonyl group of the ester. This would account for the shift to the longer wave lengths and the increase in intensity of the band associated with the carbonyl group, and it is in accord with the results of the previous investigations.[3]

The writers wish to express gratitude to Dr. E. K. Plyler for the use of his laboratory facilities.

Summary

Ethyl formate and ethyl acetate were found to shift the OH band of methyl alcohol to the shorter wave lengths and to increase its intensity. The CO band of the esters was shifted to the longer wave lengths by the alcohol, and its intensity was increased correspondingly. As a possible means of accounting for these results it was suggested that the esters may tend to decrease the polymerization of the alcohol, and to become associated with it, to some degree, through the formation of weak hydrogen bonds.

CHAPEL HILL, N. C. RECEIVED JANUARY 6, 1937

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[5] E. L. Kinsey and J. W. Ellis, *Phys. Rev.*, **49**, 105 (1936).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Pinacol Rearrangement of *cis*- and *trans*-1,2-Dimethylcyclohexanediol-1,2 and the Relationship of the Walden Inversion to the Mechanism of Molecular Rearrangements

BY PAUL D. BARTLETT AND IRVING PÖCKEL

The course of a molecular rearrangement has been observed in some cases to depend upon the conditions of the rearrangement[1] and upon the configuration of the rearranging compound.[2] The dependence of the course of reaction upon configuration in the alicyclic series has been studied hitherto only for cases of *semi*-pinacolic rearrangements such as that of 1-methylcyclohexanediol-1,2. When the *cis*-isomer of this compound forms 2-methylcyclohexanone on dehydration, it is ascribed to a direct elimination of water, molecular rearrangement occurring to an important extent only in the *trans*-isomer, where ring contraction makes the rearrangement evident.

We have undertaken the study of an actual pinacol rearrangement, where vinyl dehydration is impossible, and where the results tell us directly the effect of configuration upon the relative ease of migration of two organic radicals. There is little doubt of the configurations of the 1,2-diols in the cyclohexane series. The ultimate criterion in this series is the resolution of the *trans*-cyclopentanediol and *trans*-cyclohexanediol into optical isomers.[3] A number of independent criteria, most of them due to Böeseken and his co-workers, support the generalization that where the two isomeric diols can be prepared, one by hydration of the corresponding epoxide and the other by aqueous permanganate oxidation of the corresponding cyclohexene, the former has the *trans* and the latter the *cis* configuration. The isomeric 1,2-dimethylcyclohexanediols-1,2 have been prepared by these methods, and hence although neither of them has been resolved, their configurations are known with a high degree of probability.

The *trans*-pinacol, m. p. 92–92.5°, prepared by hydrolysis of the oxide, was rearranged by Namet-

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[1] Bartlett and Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

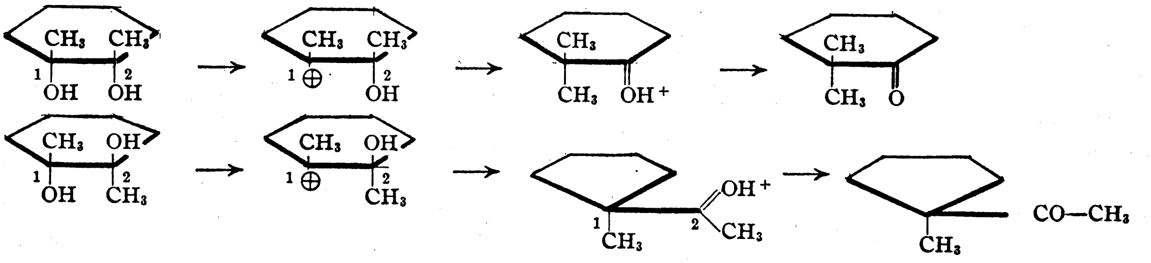
[2] Tiffeneau and Tchoubar, *Compt. rend.*, **199**, 360, 1624 (1934); *ibid.*, **202**, 1931 (1936).

[3] Derx, *Rec. trav. chim.*, **41**, 333 (1922); Van Loon, Thesis, Delft, 1929, p. 51; Helferich, Burkhardt and Hiltmann, *Ber.*, **70**, 308 (1937).

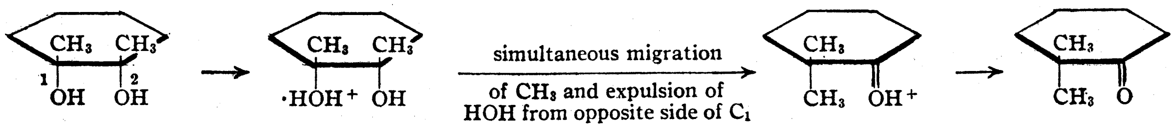
kin and Delektorsky[4] and found to give 1-methyl-1-acetylcyclopentane in 78% yield (semicarbazone, m. p. 140.5–141°). We repeated this experiment for the sake of standardizing our conditions and then, using the same procedure (boiling with 20% sulfuric acid), carried out the rearrangement of the *cis*-pinacol, m. p. 38.5–39.1°, prepared by the action of aqueous permanganate on 1,2-dimethylcyclohexene-1. The sole product of this rearrangement was 2,2-dimethylcyclohexanone, whose semicarbazone, m. p. 202–204° with decomposition, was isolated in 74% yield and unmixed with any of its lower melting isomer.

These observations have an important bearing on the mechanism of the pinacol rearrangement. This reaction is included by Whitmore among those rearrangements which proceed because a carbon atom exists with an "open sextet" of electrons,[5] which becomes completed by the migration of an organic radical with its electron pair. Despite the success of this theory in correlating facts and predicting the course of reactions, its users have been rather cautious not to speak literally of positive carbonium ions. Recently skepticism has been growing concerning the actual existence of such ions in metathetical reactions.[6]

In the present reaction we are dealing with the relative migration aptitudes of two groups, the methyl group and that group which is a part of the cyclohexane ring.



The space relations cannot be pictured exactly, since the cyclohexane ring is non-planar and the *cis* groups may be at any angle to each other within a range of angles determined by the mobility of the ring. However, the *average* positions of the groups, if the ring is mobile, are shown in the formulas. In the *cis*-pinacol, the ring carbon atom and the methyl group which migrates are about equally remote from the hydroxyl group which is eliminated in the reaction. In the *trans*-pinacol, the ring carbon atom which migrates is much more remote from the replaced hydroxyl group than the methyl. In other words, a group migrates by preference which is located in space near the ***opposite side*** of carbon atom No. 1 to that occupied by the hydroxyl group which is to be replaced. This is inconsistent with the idea that the hydroxyl group is actually removed before the migration occurs, for then the radical most accessible to the open spot on carbon No. 1 would surely be the one to migrate. The fact that different products result from the two stereoisomers also excludes the formation of a racemizable "open sextet," as do the pinacolic and semi-pinacolic deaminations of McKenzie,[7] which yield optically active products. There remains only the possibility that the migration of carbon and the expulsion of the hydroxyl are simultaneous processes. The preferred migration of the radical situated near the back side of the carbon atom No. 1 brings out a very strong resemblance between the pinacol rearrangement and those replacement reactions[8] in which it has been so elegantly shown that Walden inversion attends every act of replacement. Whether or not a Walden inversion mechanism is the only one by which a pinacol rearrangement occurs, this case in which the inversion mechanism is the preferred one seems to justify the modification of the "open sextet" theory as indicated in the scheme



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(4) Nametkin and Delektorsky, *Ber.*, **57**, 583 (1924).

(5) Whitmore, THIS JOURNAL, **54**, 3274 (1932).

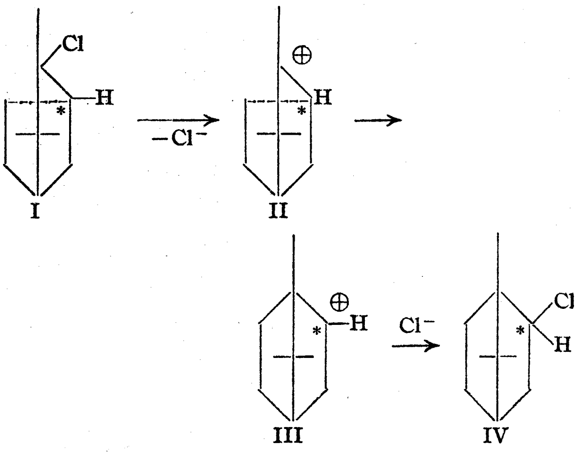
(6) Ogg, paper presented at the Symposium on Molecular Structure, Princeton, N. J., January 2, 1937; Wallis and Bowman, *J. Org. Chem.*, **1**, 383 (1936), especially p. 387.

(7) McKenzie, Roger and Wills, *J. Chem. Soc.*, 779 (1926); Roger and McKenzie, *Ber.*, **62**, 272 (1929).

(8) Olson and Long, THIS JOURNAL, **56**, 1294 (1934); Hughes, Juliusburger, Masterman, Topley and Weiss, *J. Chem. Soc.*, 1525 (1935).

A similar mechanism was written by Wallis and Bowman[6] for the more complicated case of a dehydration by thionyl chloride.

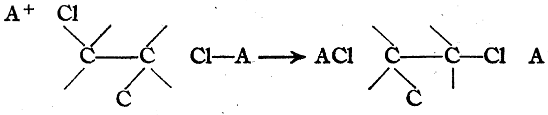
The "open sextet" theory has been of the greatest service in correlating the facts of the Wagner–Meerwein rearrangement. The extensive and careful work of Meerwein and van Emster[9] showed that the conversion of camphene hydrochloride (I) into isobornyl chloride (IV), which is promoted by solvents like sulfur dioxide, cresol, and nitromethane, and by such catalysts as hydrogen chloride, stannic and ferric chlorides, could be formulated as follows



From the standpoint of the existence of free ions, it is a most remarkable property of this rearrangement that of the two possible stereoisomeric chlorides, differing in the configuration of the starred carbon atom, only one—isobornyl chloride—is the direct product. Its isomer, bornyl chloride, is nevertheless the more favored at equilibrium, and is produced very slowly by the same reagents on long standing. The bond represented by the dotted line in the camphene formulas is, in space, behind the vertical bond which it crosses in the diagram. Therefore, if the simple ionization picture were correct, the only explanation for the formation of isobornyl chloride would be that the chloride ion caught the ion III with its open face still to the rear, in the place vacated by the migrating bond. This demands that isobornyl chloride should have the "endo" configuration, advocated by Lipp,[10] rather than the "exo" assignment of Vavon[11] and Hückel.[12] The recent work of Asahina, Ishidate and Sano[13] has shown that isoborneol in fact possesses the "exo" configuration.

It is not rigorously certain that isobornyl chloride is configuratively related to isoborneol, but all evidence points in this direction. This chloride is produced from borneol under conditions normally leading to Walden inversion.[14] Furthermore, the Wagner–Meerwein rearrangement can be duplicated with an acetate radical instead of the chlorine, by treating camphene with acetic and sulfuric acids (Bertram–Walbaum reaction), and the product in this case is isobornyl acetate, which can be hydrolyzed normally to isoborneol, almost certainly without change of configuration.

We can only conclude that the Wagner–Meerwein rearrangement involves complete Walden inversion at the starred carbon atom. This is incompatible with any reasonable deductions from the literal open sextet theory, and is equally incompatible with a series of steps involving solvated carbonium ions which undergo inversion at every reaction. It is completely compatible with a "push and pull" theory analogous to the one advanced by Lowry[15] for acid–base catalysis, in which donors and acceptors of protons are replaced by donors and acceptors of chloride ions, and a Walden inversion occurs at each replacement involving the halogen ion. Such a mechanism may be represented schematically thus



In this representation ACl is any compound capable of yielding a chloride ion, and the three carbon atoms are those three of the camphene-isobornyl system which actually participate in the rearrangement.

Meerwein and van Emster state that the rearrangement is a first order reaction, and this can of course not be literally true if the mechanism we have outlined is correct. Two observations of these authors show the way to the explanation. In the first place, hydrogen chloride is a powerful catalyst for the rearrangement;

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[9] Meerwein and van Emster, *Ber.*, **53**, 1815 (1920); **55**, 2500 (1922).

[10] Lipp, *Ann.*, **480**, 298 (1930).

[11] Vavon, *Bull. soc. chim.*, [4] **39**, 925 (1926).

[12] Hückel, *Ann.*, **477**, 157 (1930).

[13] Asahina, Ishidate and Sano, *Ber.*, **69**, 343 (1936).

[14] Wallach, *Ann.*, **230**, 231 (1885); Wagner and Brykner, *Ber.*, **32**, 2307 (1899).

[15] Lowry and Faulkner, *J. Chem. Soc.*, 2883 (1925); Lowry, *Chem. Rev.*, **4**, 231 (1927).

and in the second place, hydrogen chloride is always present in any solution of camphene hydrochloride, for this compound dissociates rapidly and reversibly into hydrogen chloride and camphene. In most of the solutions used by Meerwein the degree of dissociation was determined as being between 5 and 10%, and the dissociation equilibrium was established rapidly enough to be maintained throughout the reaction.

Now, either hydrogen chloride or the free chloride ion might act as a chloride donor, and either hydrogen chloride or solvated hydrogen ion might act as a chloride acceptor. The purpose of the present discussion is not to decide among these possibilities, but to present a recalculation of the kinetic data of Meerwein and van Emster, showing that two different kinetic formulations, based upon the "push and pull" theory, both fit these data better than the first order formulation used by the original investigators.

If x is the concentration of camphene hydrochloride, at equilibrium with a small concentration y of hydrogen chloride and of camphene, then at all times

$$y^2 = K^2x$$

where K^2 is the equilibrium constant of dissociation. In most of the solvents employed, it is proper to treat the hydrogen chloride thus as completely non-ionized, for they are solvents of far less basicity than water or the alcohols. We may now suppose two alternative kinetic situations, which are representative but do not exhaust the possibilities.

CASE I.—Suitable collision between the camphene hydrochloride and a single hydrogen chloride molecule, acting as either donor or acceptor (or a hydrogen and a chloride ion), is sufficient to bring about reaction. In this case

$$-\mathrm{d}x/\mathrm{d}t = kxy = kx \times K\sqrt{x} = kKx^{3/2}$$
$$\text{and} \qquad 1/\sqrt{x} - 1/\sqrt{x_0} = (1/2)kKt$$

where x_0 is the initial value of x.

CASE II.—The reaction is brought about by suitable collision between a camphene hydrochloride molecule and *two* hydrogen chloride molecules (one acting as donor and one as acceptor). Then

$$-\mathrm{d}x/\mathrm{d}t = kxy^2 = kK^2x^2, \qquad \text{and}$$
$$(1/x) - (1/x_0) = kK^2t$$

These assumptions lead, respectively, to 3/2-order and to second-order kinetic equations.

Meerwein and van Emster report the original data for reaction in ten solvents, of which one run, that with petroleum ether as solvent, was so slow that it was carried only to about 10% of total reaction. The other nine were followed to about 60% reaction. In order to make the fairest possible comparison between the first, three-halves, and second order formulations for these nine runs we have used the method of normal equations to pass the best straight line, in each of the twenty-seven cases, through the points which are supposed to lie on a straight line. The mean deviations of the points from the straight line have then been reduced to a common scale, with the slope of each line taken as the unit, so that the reduced mean deviations represent the fractional error in the value of k which would be made by computing k from two points an hour apart, one of which was in error by the mean deviation. This procedure eliminates the undue emphasis on the initial point of each curve which is inherent in the method used by Meerwein and van Emster.[15a] In each case the first value of k as determined by them is much lower than those determined from subsequent points. This is in accordance with the "push and pull" mechanism, which demands a short incubation period while the camphene hydrochloride is dissociating, but the least squares treatment shows that the second point is by no means so far off the curve as is suggested by the successive constants of Meerwein and van Emster.

As an example of this treatment we may show the fitting of a second order kinetic equation to the data on the rearrangement in benzene at 40°. The solution of the normal equations leads to the most probable straight line given by

$$1/x = 0.00995 + 0.0000496t$$

in which for convenience the unit of x is taken as one-hundredth of the initial concentration (Meerwein's results are tabulated in terms of per cent.). In the following table, the values in the "calculated" column are those obtained with the use of this equation.

The superiority of this formulation over the 3/2-order and first order is shown both by its lower reduced mean deviation (Table II) and by the

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(15a) Even the method used by Meerwein and van Emster leads to the same conclusions with regard to the order of the reaction. We have also applied a more exact formulation taking into account the fact that not x, but $x + y$, is the quantity whose rate of change determines the order of the reaction. This formulation also produces no change in the conclusions, and makes such a minor correction in each case that for our present purpose the simpler formulation seems preferable.

TABLE I

RATE OF REARRANGEMENT OF CAMPHENE HYDROCHLORIDE IN BENZENE AT 40°

Hours	$1/x$ (obsd.)	$1/x$ (calcd.)	Deviation × 10^5
0	0.01000	0.00995	− 5
17	.01066	.01079	+13
42	.01205	.01203	− 2
66	.01310	.01322	+12
95	.01502	.01466	−36
143	.01696	.01704	+ 8
192	.01941	.01947	+ 6
		Average	12

Reduced mean deviation = 0.00012/0.0000496 = 2.36

fact (Table I) that the deviations alternate in sign, indicating that the points are without trend, while the signs of the deviations in the other two formulations clearly indicate a curvature.

Table II summarizes the results of the comparison of formulations for the nine solvents.

TABLE II

COMPARISON OF FIRST, THREE-HALVES AND SECOND-ORDER FORMULATIONS FOR THE WAGNER–MEERWEIN REARRANGEMENT IN VARIOUS SOLVENTS

		Reduced mean deviation for order of reaction		
Solvent	Temp., °C.	First	Three-halves	Second
Chlorobenzene	40	3.17	1.16	0.79
Benzene	40	6.69	3.81	2.36
Nitromethane	20	0.12	0.06	0.05
Ethyl bromide	40	3.08	1.89	.84
Acetonitrile	20	0.52	0.15	.08
Benzonitrile	20	.97	.51	.20
Nitrobenzene	20	.40	.17	.25
Anisole	40	1.45	.54	.73
Bromobenzene	40	1.36	.58	.67

It should be mentioned that as measures of precision the reduced mean deviations as we have taken them are only horizontally comparable; multiplication for each run by the total number of hours of the run would make them vertically comparable in the table, but would not affect the comparison between different methods of formulation.

It is seen that for the first six solvents in the table the second-order formulation is the best; for the last three solvents, the three-halves order formulation is the best; and in all cases the first-order is much the worst. Further experimental work, which is being undertaken in this Laboratory, will be necessary to decide specifically the mechanism of this process, and to sort out the various types of "pushes and pulls" which might lead to these or intermediate orders of reaction.[16] Meanwhile, we can only be impressed with the excellence of the pioneer experimental work of Meerwein, which after fifteen years of accumulated experience still throws new light on this difficult problem.

Experimental

cis-1,2-Cyclohexanediol-1,2 was prepared by the method of Wallach.[17] It was crystallized from hexane with the aid of solid carbon dioxide, and melted at 38.5–39.1°.

Rearrangement of the *cis*-Pinacol.—0.43 g. of the *cis*-pinacol was boiled with 20% sulfuric acid and the product, a ketone of peppermint-like odor, was removed by steam distillation. The semicarbazone was prepared directly by allowing the product to stand with 0.34 g. of semicarbazide hydrochloride and 0.40 g. of sodium acetate in 40 cc. of water. The semicarbazone was obtained in a yield of 0.41 g. (74.2% based on the pinacol) and melted at 202–204° (dec.). 2,2-Dimethylcyclohexanone-1 and its semicarbazone have been made by Meerwein,[18] and by Auwers and Lange.[19] The melting point given by Meerwein is 200–201°. The isomeric ketone from the rearrangement of the *trans*-pinacol yields a semicarbazone melting at 140.5–141°.[20]

Summary

1. The pinacol rearrangement of 1,2-dimethylcyclohexanediol-1,2 takes different courses for the *cis*- and *trans*-isomers, a carbon atom migrating in each case which is, on an average, remote in space from the adjacent hydroxyl group which it replaces.

2. An interpretation of the pinacol rearrangement as involving Walden inversion at the carbon atom where replacement occurs is derived from these facts.

3. The modification of the "open sextet" theory so introduced, if extended to the Wagner–Meerwein rearrangement of camphene hydrochloride into isobornyl chloride, is consistent with the configurations of borneol and isoborneol recently assigned by chemical methods, while a literal "open sextet" theory is not.

4. It now becomes necessary to regard this Wagner–Meerwein rearrangement, not as a spontaneous intramolecular process, but as one involving donors and acceptors of chloride ion, quite analogous to the acid–base catalysis of Lowry.

5. A thorough recalculation of the kinetic data of Meerwein and van Emster shows that

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(16) A hydrogen ion as acceptor and a hydrogen chloride molecule as donor would lead to a reaction of the 7/4 order.

(17) Wallach, *Ann.*, **396**, 280 (1913).

(18) Meerwein, *ibid.*, **405**, 143 (1914).

(19) Auwers and Lange, *ibid.*, **401**, 321 (1913).

(20) Nametkin and Delektorsky, *Ber.*, **57**, 583 (1924).

either a three-halves order or a second order formulation of this rearrangement, derivable from the donor-acceptor theory, will fit the facts better than the first-order formulation used by these authors.

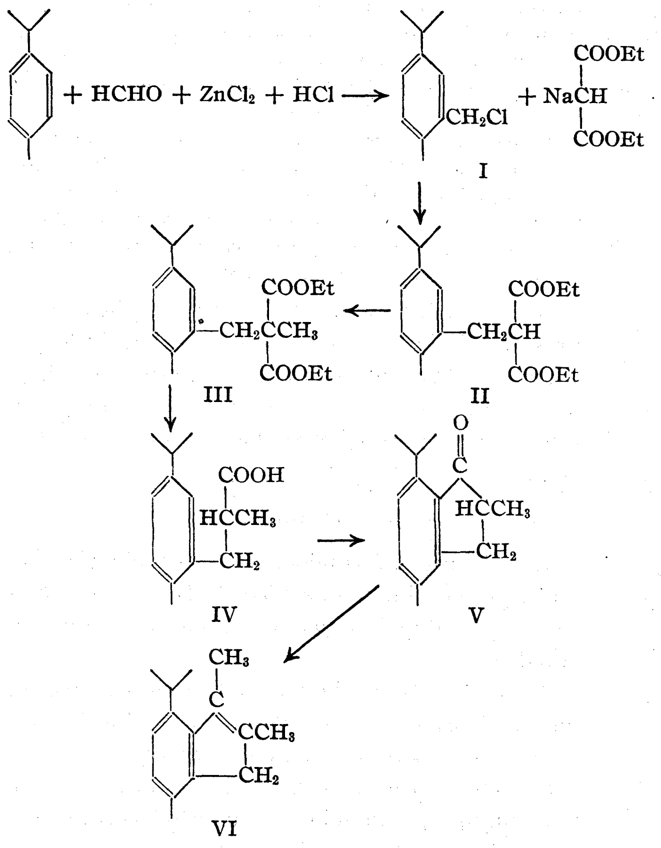
CAMBRIDGE, MASS. RECEIVED MARCH 8, 1937

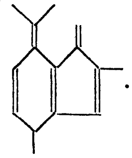
[CONTRIBUTION FROM THE NEW ZEALAND COÖPERATIVE RENNET CO., LTD.]

The Synthesis of 1,2,4-Trimethyl-7-isopropylindene

BY WALTER G. WHITTLESTON

The following equations represent the manner in which the synthesis of 1,2,4-trimethyl-7-isopropylindene was carried out



The synthesis was carried out with the object of producing a substance which on reduction and dehydrogenation would yield a compound of the structure .

Owing to shortage of materials and time, this was not completed.

The Introduction of the Chloromethyl Group into *p*-Cymene.—The first method attempted was that of Rapson and Short[1] in which *p*-cymene, anhydrous zinc chloride and paraformaldehyde were stirred into an emulsion and dry hydrogen chloride bubbled through the rapidly stirred mixture. This method was unsuccessful. It may be mentioned here that the yield obtained by the above authors, calculated on the basis of the amount of *p*-cymene taken at the start of the preparation, was 43%, and not the higher figure which they give.

The method due to Blanc[2] was finally employed, 40% aqueous formaldehyde being used in the place of paraformaldehyde. By employing apparatus in which the hydrogen chloride was distributed to the reaction mixture by a rapidly rotating hollow paddle stirrer, and keeping the temperature at 60° in a thermostatic bath, together with the use of nickel chloride as a catalyst, it was possible to get better yields than those of Blanc. The use of a small amount of nickel chloride reduced the production of tarry by-products in the reaction, and so made it much more efficient and convenient.

The preparation of diethyl methyl-(2-*p*-cymylmethyl)-malonate was carried out using the usual methods. This substance was saponified and decarboxylated. The acid chloride was prepared by the use of thionyl chloride, and after removal of the hydrogen chloride and sulfur dioxide by boiling, ring closure was effected by the addition of anhydrous aluminum chloride. The resultant ketone on treatment with methylmagnesium iodide gave 1,2,4,-trimethyl-7-isopropylindene.

Experimental

All temperatures are uncorrected. I. 2-*p*-Cymylmethyl Chloride.—Fifty grams of *p*-cymene, 20 g. of zinc chloride (anhyd.), 1 g. of nickel chloride and 40 g. of 40% formalde-

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[1] Rapson and Short, *J. Chem. Soc.*, 128 (1933).

[2] Blanc, *ibid.*, Ai, 549 (1923).

hyde were stirred together, and hydrogen chloride passed through, a temperature of 60° being maintained. After eight hours, the reaction mixture was steam distilled.

It was found better to use the small quantities mentioned, and to carry out many preparations, rather than to use larger quantities. Automatic apparatus requiring little attention facilitated the use of long reaction times; yield, 47 g. (69%) of a colorless liquid; b. p. 123–124° (20 mm.). A Stepanov chlorine determination gave 19.8% chlorine ($C_{11}H_{15}Cl$ requires 19.5%).

II. Diethyl (2-*p*-Cymylmethyl)-malonate.—Six grams of sodium was dissolved in a benzene solution of 40 g. of malonic ester, and 44 g. of 2-*p*-cymylmethyl chloride added. After boiling until the sodio derivative had disappeared, the reaction mixture was treated with water, and the benzene layer separated, dried and distilled. The required ester had a b. p. of 190–195° (9 mm.); yield 55 g. (60%).

III. Diethyl Methyl-(2-*p*-cymylmethyl)-malonate.—Four grams of sodium was dissolved in a benzene solution of 40 g. of *p*-cymylmethylmalonic ester. When the sodium had dissolved, 24 g. of methyl iodide was added. After boiling for two hours, the mixture was treated as in II; yield 32 g. of material (76%); b. p. 182–187° (8.5 mm.).

IV. Methyl (2-*p*-Cymylmethyl)-malonic Acid.—Twelve and eight-tenths grams of sodium was dissolved in 256 cc. of rectified spirits, and 48 g. of methyl (2-*p*-cymylmethyl)-malonic ester was added. After refluxing for four hours, the mixture was diluted with water and the excess alcohol distilled off. The aqueous solution of the sodium salt was extracted with ether and then acidified with hydrochloric acid. The organic acid was separated by filtration and dried in a vacuum desiccator, yield 95%.

The dibasic acid, after careful heating over a gauze followed by distillation at 12 mm., gave an oily liquid of b. p. 189–190° (12 mm.).

2-*p*-Cymylpropionic acid was prepared in the same way as the above, but omitting the introduction of a methyl group (step III). The corresponding dibasic acid in this case was a solid of m. p. 165°. On decarboxylation, a crystalline monobasic acid of b. p. 190–195° (20 mm.), and m. p. 76.5° was obtained. Equivalent weight by titration 210; by silver salt analysis 205.7 ($C_{13}H_{18}O_2$ requires 206.0).

The 3-*p*-cymylpropionic acid obtained by Cook, *et al.*,[3] has a m. p. of 61–62°. This indicates that the chloromethyl group definitely enters position 2 as has been supposed, in the initial synthesis.

V. 2,4-Dimethyl-7-isopropylhydrindone.—2-*p*-Cymylisobutyryl chloride was prepared by treating 20 g. of the isobutyric derivative with 15 g. of thionyl chloride dissolved in petroleum ether free from aromatic hydrocarbons. After keeping at 60° for two to three hours, the temperature was raised, thus removing the sulfur dioxide and most of the hydrogen chloride formed.

The acid chloride was not isolated, but 12 g. of anhydrous aluminum chloride was added slowly. The product was heated on the water-bath for two to three hours, decomposed with dilute hydrochloric acid, and extracted with petroleum ether. Distillation yielded 15 g. of material, b. p. 147–150° (9 mm.). It was not found possible to crystallize the product which appeared to be contaminated with a highly colored impurity of similar boiling point.

VI. 1,2,4-Trimethyl-7-isopropylindene.—One and two-tenths grams of magnesium was dissolved in 6.0 g. of methyl iodide in anhydrous ether, and 8 g. of the ketone added. This reaction yielded 4 g. of a substance, which, on recrystallization from absolute ethanol, formed colorless, silky, acicular crystals with a high refractive index. The substance melted at 99.5°, and boiled with slight decomposition at 140–145° (10 mm.).

Analysis gave C, 89.7; H, 10.07. ($C_{15}H_{20}$ requires C, 90.0; H, 10.0.) This indicates that the elements of water have been lost, yielding the corresponding unsaturated indene derivative. The substance was found to absorb bromine readily, and to form a picrate consisting of fine, brick-red, acicular crystals, m. p. 88–89°.

Acknowledgments.—The author wishes to express his indebtedness to the late Dr. J. K. H. Inglis for his suggestions and kindly criticism. The work was carried out at Otago University during the tenure of a Sir George Grey Scholarship.

Summary

1. The use of formaldehyde, hydrochloric acid, and zinc chloride in the introduction of the chloromethyl group into *p*-cymene has been investigated.

2. It has been shown that with the use of nickel chloride as a catalyst, the yields in this reaction can be improved considerably.

3. The synthesis of 2-*p*-cymylisobutyric acid, 2-*p*-cymylpropionic acid, 2,4-dimethyl-7-isopropylhydrindone, and 1,2,4-trimethyl-7-isopropylindene has been carried out.

ELTHAM, NEW ZEALAND RECEIVED NOVEMBER 19, 1936

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[3] Cook, *et al.*, *J. Chem. Soc.*, 1727 (1934).

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

Photochemical Investigations. III. The Effect of Cell Size on the Quantum Yield for the Decomposition of Ammonia[1]

BY EDWIN O. WIIG

Recently suggested mechanisms[2-4] for the photolysis of ammonia are based on experimental data which apparently show the quantum yield independent of pressure. However, a later investigation[5] demonstrated that there is a change in the quantum efficiency with a change in the total ammonia pressure. This dependence might be due to a change in the character of the homogeneous gas reactions occurring after the primary dissociation brought about by light or to a change from a homogeneous reaction to a heterogeneous reaction taking place on the walls of the reaction cell. As the thermal decomposition of ammonia is known to be heterogeneous and probably involves hydrogen atoms and NH,[6] one might be inclined to be suspicious of the photo-reaction in the absence of evidence of homogeneity or heterogeneity. In view of this, no mechanism accounting for the pressure dependence of the yield was suggested in the previous paper.[5] The experiments reported here were carried out in a reaction cell of somewhat different size from that previously used in an attempt to settle this point.

Experimental Details

The light source, apparatus and materials were the same as used earlier,[5] except for the replacement of the previous cell by another. Both cells were cylindrical with plane parallel windows on the ends and all seams fused. The first cell (Cell 1) was 25 mm. in diameter by 50 mm. long with an area–volume ratio of 200 mm.$^{-1}$ while the new cell (Cell 2) was 40 mm. in diameter and 35 mm. long with an area–volume ratio of 157 mm.$^{-1}$. At the conclusion of the experiments with each cell the rear window was cut off and its transmission measured. Previous to removing the windows, hydrogen bromide was decomposed in the cells, using exactly the same procedure as in ammonia photolysis.

Results

In order to compare the photolyses in the two cells the quantum efficiency for the ammonia decomposition was determined, as in the earlier work, for the single Zn line λ 2100 Å. at ammonia pressures ranging from 4–886 mm. The results are shown in Table I. These yields were calculated on the assumption that the non-condensable gas remaining after freezing out the ammonia with liquid air consisted of 75% hydrogen and 25% nitrogen. The energy measurements upon which these quantum yields depend were checked by measuring the quantum efficiency for the decomposition of hydrogen bromide. Using the experimentally determined correction factors for the energy losses at the cell window, lens and

TABLE I

PHOTOLYSIS OF AMMONIA IN CELL 2

λ 2100 Å. Volume, 215 cc. Room temp. 24–30°

Expt.	P_{NH_3}, mm.	Exposure, sec.	Quanta absorbed $\times 10^{-14}$	$P_{N_2+H_2}$ microns	Quantum yield
B-32	4	1920	276	0.56	0.072
31	9	1740	481	1.53	.114
15	12	1380	355	0.81	.081
30	15	1740	616	2.81	.163
29	18	1560	378	1.97	.185
14	22	1320	556	2.96	.189
28	28	1800	716	4.49	.222
27	35	1800	706	4.45	.224
13	43	1440	741	4.99	.242
26	54	1380	713	4.87	.243
25	65	1745	969	7.01	.259
12	83	1200	628	4.53	.257
24	93	1380	966	7.01	.259
23	100	1260	636	4.16	.232
17	109	1440	777	5.27	.242
22-B	120	900	502	3.72	.263
16	130	1380	652	4.64	.251
22-A	173	1500	827	5.58	.239
11	204	1620	820	5.31	.229
21	211	1380	867	5.68	.231
20	326	1500	1040	6.11	.207
10	390	1320	671	4.16	.218
19	454	1500	1140	6.11	.192
18	520	1200	668	3.12	.165
33	608	1200	710	3.21	.160
36	673	1500	1070	4.75	.158
34	742	1320	807	3.70	.163
37	812	1500	851	3.44	.144
35	886	1560	1080	4.02	.142

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(1) Presented in part at the Schenectady and Troy, N. Y., Intersectional Meeting of the American Chemical Society, October 25–26, 1935.

(2) Wiig and Kistiakowsky, THIS JOURNAL, **54**, 1806 (1932).

(3) Ogg, Leighton and Bergstrom, *ibid.*, **56**, 318 (1934).

(4) Farkas and Harteck, *Z. physik. Chem.*, **B25**, 257 (1934).

(5) Wiig, THIS JOURNAL, **57**, 1559 (1935).

(6) Frankenburger, *Z. Elektrochem.*, **39**, 97 (1933).

thermopile window, the average quantum yield found for the hydrogen bromide photolysis was 2.14. This is in good agreement with the value of 2.01 found by experiment in the previous investigation and with the accepted value of 2.0. The results with hydrogen bromide given in Table II have been corrected to make the average yield 2.00 and the data for ammonia in Table I have been corrected similarly. The correction is small and might have been neglected but it serves to refer the data in Cells 1 and 2 to the same standard. All the experiments performed have been listed in these two tables except runs B1–9 which were performed on old hydrogen bromide that had been stored in contact with phosphorus pentoxide for several months. The yields in these experiments were very erratic. The later experiments of Table II, as in the earlier work, were carried out with freshly prepared hydrogen bromide which, as may be seen, gave easily reproducible results.

TABLE II

PHOTOLYSIS OF HYDROGEN BROMIDE IN CELL 2

λ 2100 Å. Room temp. 26–28°

Expt.	p_{HBr}, mm.	p_{H_2}, total, microns	p_{H_2}, thermal, microns	Quantum yield
B-40	54	16.13	1.74	1.95
41	54	14.27	1.40	1.99
38	58	10.61	1.28	1.95
39	58	10.04	1.18	2.15
42	64	18.56	1.88	1.97
			Av.	2.00

From Table I it is apparent that the same sort of pressure dependence of the yield obtains as in the earlier cell. For convenience of comparison the data in Table I of the earlier work[5] and the present data have been plotted as shown in Fig. 1. The full curve is the curve in Fig. 2 of the preceding paper[5] and shows the variation of quantum yield with pressure in experiments performed with Cell 1. The vertical lines, which correspond in length to a quantum yield of 0.025 and whose mid-point is the actually determined value, represent the individual experiments in Cell 2 as given in Table I. Some measurements made with a third cell (Cell 3) of the same diameter as Cell 1 but 100 instead of 50 mm. long gave yields which fit the curve for Cell 1.

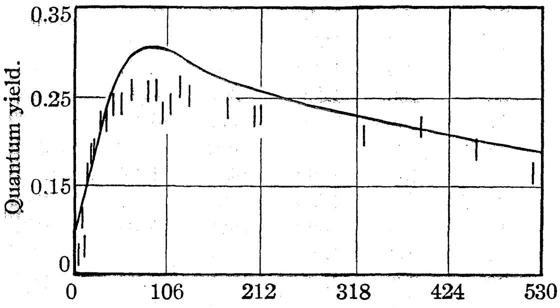

Fig. 1.—Quantum yield for the photo decomposition of ammonia as a function of pressure at λ 2100 Å.: full curve, cell 1; vertical lines, cell 2.

After the completion of this work there appeared a paper by Welge and Beckman[7] reporting an investigation of the photodecomposition of ammonia in the region of very minute amounts of decomposition. Their results show that in their apparatus at pressures of products of 0.05 mm. or greater the non-condensable gases consist of 75% hydrogen and 25% nitrogen, but when the amount of decomposition is decreased down to pressures less than 1 micron the gas contains about 95% hydrogen and approaches 100% as a limit. Based on the percentage of hydrogen and that the stoichiometric reactions involved are

$$2NH_3 = N_2 + 3H_2 \text{ and}$$
$$2NH_3 = N_2H_4 + H_2$$

Welge and Beckman find quantum yields approaching unity. They suggest that perhaps the low quantum yields obtained by others[2,3,5] are due in part to a change in composition of the gaseous products.

In the experiments of Wiig and Kistiakowsky the products were shown to be $3H_2 + N_2$ down to 8 μ pressure with the full light of the zinc spark and down to 16 μ with the monochromatic light and conditions used in the quantum yield determinations. The amount of decomposition in every experiment with λ 2090 Å. corresponded to a pressure of products of 19.7 μ or greater. The quantum yields of *ca.* 0.25 obtained are based, therefore, on a known composition of products and are real. In the present studies the products of the exposure of ammonia to the full light of the zinc spark were shown[5] to be 75% hydrogen and 25% nitrogen down to pressures of 22 μ. The pressures of the decomposition products in the data used here vary from about 0.6–12 μ.

Subsequently, the constancy of the composition of the products down to about 2 μ pressure has

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(7) Welge and Beckman, THIS JOURNAL, 58, 2462 (1936).

been tested. If the non-condensable product at 1 μ is 100% hydrogen, the calculated quantum yield on the assumption of 75% hydrogen and 25% nitrogen would be[7] about 0.25. The maximum value of the yield (Fig. 1) comes at an ammonia pressure of about 100 mm. and has a value of about 0.30 in Cells 1 and 3 for λ 2100 Å. and *ca.* 12 μ of products. If this efficiency is for products containing $3H_2 + N_2$, then on reducing the time of exposure so as to obtain only 1 μ of products the calculated yield should approach 0.25 as the gas approaches 100% hydrogen. Cell 3, as it is the only one intact, was used for making the test. The cadmium line at λ 2144 Å. was chosen since decompositions up to 30 μ could be obtained readily with the higher intensity available. The results are given in Table III.

TABLE III

PHOTOLYSIS OF AMMONIA IN CELL 3

λ 2144 Å. P_{NH_3} = 105 mm. Vol. = 230 cc. Temp., 21–27°

Expt.	Exposure, sec.	Quanta absorbed, $\times 10^{-14}$	Pressure of products, microns	Quantum yield
C-135	2580	3236	29.96	0.354
136	2220	2320	21.81	.360
142	2100	976	8.44	.332
139	600	725	6.55	.344
143	1500	621	5.60	.349
140	360	454	4.12	.345
141	180	230	1.73	.288
138	180	185	1.30	.266
137	120	137	0.98	.274

These yields at λ 2144 Å. are slightly higher than those reported for λ 2100 Å. The data of Ogg, Leighton and Bergstrom show the same tendency to higher values at λ 2144 as compared with λ 2100 Å. Whether or not this difference is real is of no importance here. The yield, it will be observed from Table III, is about 0.345 for products varying from 30 μ, where the composition has been determined with certainty, down to 4 μ. At pressures of products less than 2 μ the yield falls sharply which, on the basis of Welge and Beckman's results, might indicate a change in composition. All the experiments indicated in Fig. 1 produced more than 4 μ of non-condensable gas except a few runs at low or high pressures where the yields are less than 0.20 (*e. g.*, *ca.* 0.10 in Expts. B-15, 31, 32). If the gas were 100% hydrogen in these few experiments, the yield should still be about 0.25, so that a change in composition cannot account for these low yields.[8] It seems, therefore, that the variation in quantum yield at ammonia pressures ranging from at least 30–700 mm. is real and not due to a change in composition of gaseous products. In the decomposition of ammonia by α-particles, Luyckx[9] likewise finds an increase in the yield per ion pair as the ammonia pressure is decreased to about 100 mm. and points out that earlier data[2,10] show the same tendency, although no such claim was made.

Discussion

The plot in Fig. 1 shows a small but very definite difference in the quantum yields in the two cells at about 60–300 mm. ammonia pressure. In this pressure range the reaction apparently becomes heterogeneous. The experiments of Welge and Beckman[7] also indicate that the reaction must be at least partly a wall reaction, since saturation of the walls with atomic hydrogen previous to photolysis results in a higher yield. By means of the effect of hydrogen atoms on the para- to ortho-hydrogen transformation Farkas and Harteck[4] have shown that the hydrogen atom concentration, [H], in ammonia undergoing photolysis, decreased with decrease in total pressure for total ammonia and hydrogen pressures less than 140 mm. When the surface was increased by filling the reaction cell with lengths of quartz tubing, [H] decreased. While these experiments were performed at 400 and 300°, respectively, and not at room temperatures, they nevertheless indicate the heterogeneous character of the reaction.

The dependence of the quantum yield on ammonia pressure is readily accounted for by making use of the following reactions. The individual reactions have been suggested at various times but not as presented here.

$$\begin{array}{rll}
NH_3 + h\nu \longrightarrow (NH_3)' & \longrightarrow NH_2 + H & (1) \\
H + H \text{ at wall} & \longrightarrow H_2 & (2) \\
NH_2 + H + M & \longrightarrow NH_3 + M & (3) \\
NH_2 + NH_2 + M & \longrightarrow N_2H_4 + M & (4) \\
NH_2 + NH_2 & \longrightarrow N_2 + 2H_2 & (5) \\
N_2H_4 + H & \longrightarrow NH_3 + NH_2 & (6)
\end{array}$$

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(8) There is a striking difference in the intensities used in the experiments of Welge and Beckman and those in Fig. 1. In the latter the number of quanta absorbed varies from 300 to 1300 × 10^{14}, the smaller number coming at low ammonia pressures, where absorption is weak. The average is about 800 × 10^{14}. For approximately the same exposures, the number of quanta absorbed in the experiments of Welge and Beckman varies from 41–86 × 10^{14}, the average being 60 × 10^{14}. Whether or not this accounts for the difference in the composition of the products obtained in the two investigations is difficult to state.

(9) (a) Luyckx, *Bull. soc. chim. belg.*, **43**, 117 (1934); (b) Luyckx, Revue de Questions scientifiques, Nov., 1935, p. 441.

(10) Kuhn, *J. chim. phys.*, **23**, 521 (1926).

The evidence for reaction (1) is cited by numerous workers.[2–4,7] Farkas and Harteck, as well as Welge and Beckman, have suggested that the union of hydrogen atoms, (2), is a wall reaction. Reactions (3) and (4) followed by (6) account for the decrease in rate observed by Melville.[11] As pointed out by Taylor and Jungers,[12] reaction (3) (and also (4) followed by (6)) provides one reason for the low quantum yield in ammonia photolysis, and also accounts for the NH_2D and NHD_2 which they found in mixtures of ammonia, deuterium and mercury vapor exposed to a quartz mercury arc. The presence of hydrazine, as demanded by reaction (4), has been shown by various investigators.[7] The reaction between hydrazine and hydrogen atoms, (6), has been shown experimentally by Dixon[13] to proceed rapidly. The exact nature of this reaction is open to question,[2,3,9,14] but reaction (6) as given here appears to be probable.[3] The NH_2 formed in (6) disappears in (3), (4) or (5), and the equations may readily be combined to give the observed reaction products, $3H_2 + N_2$.

As the ammonia pressure is decreased from about one atmosphere down to about 100 mm. reactions (2) and (5) would be favored as against (3), (4) and (6) and the quantum yield should increase. At the maximum, as the different yields in the two cells indicate, the reaction becomes heterogeneous and regeneration of ammonia can now begin to occur at the walls. Thus, a rapid fall in yield is to be expected as the wall effect increases, which is in agreement with observation. The above mechanism leads to the rate equation

$$-\mathrm{d}(\mathrm{NH_3}) = \frac{I_{\mathrm{abs.}}\sqrt{k_2(k_5 - k_4M)}}{k_3M + k_5\sqrt{\dfrac{k_2}{k_5 - k_4M}}}$$

which should hold for pressures greater than about 100 mm.; below that the reaction is both homogeneous and heterogeneous, the proportions of each depending on the pressure. At high pressures k_2 would involve three-body collisions, at intermediate pressures three-body collisions and wall reaction. The rate, it will be observed, is proportional to the energy absorbed and the quantum yield independent of light intensity, which is in agreement with observation[2,4,15] for the intensities used. As the pressure is increased above 100 mm. the denominator in the above equation increases more rapidly than the numerator and the quantum yield falls. For moderately high pressures (1.2 to 8.5 atmospheres) as in the experiments of Ogg, Leighton and Bergstrom the quantum yield would probably change very little. When the value of M attains very large values as in liquid ammonia or aqueous solutions of ammonia, the rate approaches zero. This is in agreement with the observed facts as both liquid ammonia[16] and aqueous solutions of ammonia[17] undergo no appreciable photodecomposition. The suggested mechanism also explains the lower yield in the larger cell, Cell 2, since diffusion of hydrogen atoms to the walls would be slower.

From the proposed mechanism one would predict that the addition of an inert gas to ammonia at a pressure of about 100 mm. should result in a decreased quantum yield. Likewise, the addition to ammonia at pressures of 10–40 mm. of a foreign gas so as to make the total pressure about 100 mm. should give an increased yield. These effects would account for Warburg's constant quantum yield of 0.23 at total pressures of ammonia, nitrogen and hydrogen of 800–900 mm. The work is being continued with a view to testing these and other points.

Summary

The quantum efficiency for the photolysis of ammonia by λ 2100 Å. is found to depend upon the size of the reaction cell, being slightly, but definitely, smaller in a cell of larger diameter. The reaction appears to become heterogeneous at ammonia pressures less than about 300 mm. and may be partly heterogeneous at higher pressures. A mechanism for the photodecomposition is suggested and discussed.

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(11) Melville, *Trans. Faraday Soc.*, **139**, 885 (1932).

(12) Taylor and Jungers, *J. Chem. Phys.*, **2**, 452 (1934).

(13) Dixon, THIS JOURNAL, **54**, 4262 (1932).

(14) Elgin and Taylor, *ibid.*, **51**, 2059 (1929); Wenner and Beckman, *ibid.*, **54**, 2787 (1932).

(15) Unpublished results in this Laboratory.

(16) Ogg, Leighton and Bergstrom, THIS JOURNAL, **55**, 1754 (1933).

(17) Kuhn, *Compt. rend.*, **178**, 708 (1924).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Heats of Organic Reactions. V. Heats of Hydrogenation of Various Hydrocarbons

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In the previous publications of this series[1] there have been reported the heats of hydrogenation of a considerable number of unsaturated hydrocarbons. These data, it has been shown, indicate some rather striking regularities, correlating molecular structure and this thermo quantity. In this paper we shall present some additional determinations and attempt to substantiate and to amplify some of our earlier generalizations. Our next paper will deal with hydrogenations of some oxygen-containing compounds.

Preparation of Materials

Inasmuch as the purity of the compounds is probably the factor limiting the accuracy of our calorimetric determinations, we shall follow our set precedent and report the preparations in some detail.

Ethylbenzene.—Ethylbenzene was prepared from acetophenone by the method of Clemmensen.[2] Fritche's acetophenone was distilled through Column B of Paper II at 100 mm. pressure. The major portion, which distilled at 132.4–132.7°, was used in this synthesis. The refractive indices of the fractions collected varied from $n^{17.5}_{\mathrm{D}}$ 1.5348 to 1.5350.[3]

The best yield of crude ethylbenzene on any one reduction was 50% of the theoretical; the over-all yield of crude material from 2280 g. of actophenone was 42.5%. The crude product was washed with potassium carbonate solution, dried over calcium chloride and let stand over sodium for fifteen hours. It was then distilled from the sodium, giving 769 g. of product which was fractionated in Column B; 686 g. of material was obtained which distilled at 136.80 ± 0.05° at 755 mm. This corresponds to a yield of 38% based on the weight of acetophenone used. Upon refractionation through Column A of Paper II a middle fraction of 114 g. distilled at 135.97° at 765 mm. The freezing point of this fraction was −94.7°[4] and n^{20}_{D} 1.4960.[4]

The total distillate of this fractionation (approximately 515 g.) distilled at 135.98 ± 0.02° at 765 mm.

***o*-Xylene.**—*o*-Xylene ("reinst"), as obtained from Dr. Frankel and Dr. Landau of Berlin, Germany, was fractionated through Column A. The fraction chosen for calorimetric measurements, No. 5, had the following constants: b. p. 144.07–0.08° at 765 mm.,[5] n^{20}_{D} 1.5055, f. p. −25.10°.

Fraction No. 5, 90 g., was the only fraction obtained with a flat boiling point; the other fractions were lower boiling and comprised about 66% of the charge of 500 g.

Mesitylene.—Eastman best grade of mesitylene was purified according to the method given in "Organic Syntheses";[6] 398 g. of mesitylene was recovered from 500 g. of starting material. This was distilled through Column B at 100 mm.; a middle fraction of 323 g. was obtained which distilled flatly at 99.3°; n^{20}_{D} 1.4995;[7] f. p. −51.4°.[8]

Styrene.—Styrene was prepared from phenylethyl alcohol by the method of Sabetay:[9] 2074 g. of phenylethyl alcohol in two and three molar runs was dehydrated by heating over a molten 50–50 mixture of sodium and potassium hydroxides (50 g. mixture per mole of alcohol) contained in a round-bottomed flask bearing a downward condenser. Heating was so regulated that the temperature of the distillate did not exceed 140°. The product was separated from the water layer, washed with saturated calcium chloride solution and dried over calcium chloride. Treatment with metallic sodium seemed to cause considerable polymerization, so this procedure was omitted after the first three runs. The yield of styrene to this point was 1627 g. or 92%. Fractionation of the crude material from a small amount of hydroquinone through Column B at 60 mm. gave 1008 g. of material distilling at 66.7 ± 0.05° corresponding to a yield of 57% based on the phenylethyl alcohol used. The refractive indices of the fractions obtained varied from $n^{17.2}_{\mathrm{D}}$ 1.5479 to 1.5483. This material was stored over hydroquinone in the dark and redistilled as needed for the calorimeter.

Sample No. 1, 173 g., distilled at 65.15° at 50 mm.; n^{20}_{D} 1.5470.[10] Sample No. 2 distilled at 65.6° at 50 mm.; n^{20}_{D} 1.5470; f. p. −30.5°.[11]

Indene and Hydrindene.—A pure grade of indene, obtained from Gesellschaft für Teerverwertung, was distilled through Column B; the middle fraction, consisting of Samples 2, 3 and 4, had a flat b. p. of 83.8° at 30.5 mm. The refractive index of the three samples was the same, $n^{19.8}_{\mathrm{D}}$ 1.5767.[12] Sample No. 2 had a f. p. of −1.67°.[13]

Part of this fraction was hydrogenated, using the Adams catalyst,[14] to hydrindene using no solvent. Hydrogen was taken up at the rate of about nine liters an hour when 1 g. of catalyst was used for 200 g. of indene. The absorption of hydrogen ceased immediately when the calculated

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(1) I. Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935); II. Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935). III, IV, *ibid.*, **58**, 137, 146 (1936).

(2) Clemmensen, *Ber.*, **46**, 1838 (1913).

(3) Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **84**, 20 (1911), give $n^{17.2}_{\mathrm{D}}$ 1.5350.

(4) "I. C. T.," Vol. I, p. 219, gives f. p. −92.8°; b. p. 136.5° at 776.7 mm. Brühl, *Ann.*, **235**, 12 (1886), gives n^{20}_{D} 1.49594. Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1548 (1930), give −95.1° (178.0°K.). Timmermans and Martin, *J. chim. phys.*, **23**, 247(1926), give −94.4°.

(5) "I. C. T.," Vol. I, p. 219, gives for *o*-xylene: b. p. 144°, m. p. −27.1°, p. 277, n^{20}_{D} 1.5058; Rossini, *Bur. Standards J. Research*, **11**, 555 (1933), gives f. p. −25.3°.

(6) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc. 1931, p. 334; note 8, p. 337.

(7) Auwers, *Ann.*, **419**, 92 (1919), gives $n^{17.1}_{\mathrm{D}}$ 1.49804.

(8) "I. C. T.," Vol. I, p. 228, gives −52.7°.

(9) Sabetay, *Bull. soc. chim.*, [4] **45**, 69 (1929).

(10) Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **82**, 99 (1910), give n^{20}_{D} 1.5449.

(11) Waterman and de Kok, *Rec. trav. chim.*, **53**, 1133 (1934), give f. p. −33°; n^{20}_{D} 1.5462.

(12) Spilker and Dombrowky, *Ber.*, **42**, 572 (1909), give $n^{18.5}_{\mathrm{D}}$ 1.5773; Ruzicka and Peyer, *Helv. Chim. Acta*, **18**, 676 (1935), give n^{21}_{D} 1.5748.

(13) Weissgerber, *Ber.*, **42**, 569 (1909), gives f. p. −2°.

(14) Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

amount had been taken up. Practically all of the hydrindene distilled flatly in Column B at 79.0° and 29 mm.; $n^{20.7}_{\mathrm{D}}$ 1.5382;[15] f. p. −51.4°.

Cyclopentene.—Cyclopentanone was prepared from adipic acid by the method of Boedtker[16] with a 90% yield of crude product after it had been washed with potassium carbonate to remove any adipic acid and dried over anhydrous potassium carbonate. The cyclopentanone was fractionated carefully in Column B. The fractions used distilled from 130.2–130.3° at 756 mm.

Cyclopentanol was prepared from cyclopentanone by reduction with the Adams platinum catalyst. It was found that by promoting the catalyst with a small amount of iron[17] the ketone could be reduced very rapidly if the very pure ketone with no solvent was used in the Adams machine. The rate of absorption of hydrogen was about eight liters per hour. Five-tenths gram of catalyst was employed with each two-mole run. The cyclopentanol thus obtained was distilled in Column B giving a middle fraction boiling at 139.8–139.9° at 751 mm.

Cyclopentene was prepared by dehydrating the alcohol with anhydrous oxalic acid,[17a] washing the product with water and potassium carbonate solution, drying with calcium chloride and finally distilling from sodium metal. A yield of 83% based on alcohol dehydrated was obtained. The cyclopentene was then fractionated in Column A. The fraction used for measurement had the following physical constants: b. p. 44.17 ± 0.01° at 760 mm.; f. p. −134.6°; $n^{20.3}_{\mathrm{D}}$ 1.4223.[18]

α-Phellandrene.—The Hercules Powder Company through Dr. E. R. Littmann very kindly supplied us with approximately 250 cc. of α-phellandrene; the material was represented as being the best obtainable. This was purified, following the suggestions of Littmann, by distillation through a three-foot (91-cm.) jacketed, indented column under a pressure of 16 mm. The bulk of the material, about 200 cc., distilled at 62.5–66.5°. This was refluxed for one-half hour over clean metallic sodium and redistilled under 16 mm. pressure, giving a main fraction of b. p. 62.7–64.1°. A second distillation gave a main fraction of 75 cc., b. p. 64.7–65.7°; n^{20}_{D} 1.4746.[19]

α-Terpinene.—This compound, also supplied by the Hercules Powder Company, was purified in the same way as was α-phellandrene. The middle fraction from the distillation was taken for calorimetric measurement; it distilled at 81.5–82.0° under 30 mm. pressure; n^{20}_{D} 1.4757.[20]

Limonene.—Eastman best grade of limonene was distilled through Column B giving a middle fraction, Samples II, III and IV, with b. p. 74.7° at 24 mm. α-Phellandrene, α-terpinene and limonene all formed glasses when chilled in liquid air and no freezing points could be obtained. Sample II had a refractive index of n^{20}_{D} 1.4721 and for Sample IV n^{20}_{D} 1.4727 was found.[21]

Isopropylethylene.—The sample of isopropylethylene was kindly supplied by Dr. E. P. Carr of Mt. Holyoke College. The constants submitted with the sample were: b. p. 20.18–.21° at 760 mm. and n^{20}_{D} 1.3675.[22] No freezing point was obtained on this material as it formed a very viscous liquid in liquid air even after repeated warming and cooling; this agrees with the observation of Norris and Reuter.[22]

Neo-amylethylene.—This compound was prepared from the Grignard reagent of *t*-butyl chloride and allyl bromide according to the method of Whitmore and Homeyer.[23] The allyl bromide used was a flat cut at 69.75° and 753 mm. The *t*-butyl chloride was of the same grade as was used in making *t*-butylethylene. A 63% yield of the ethylene was obtained, boiling at 71.0–72.8°. This was converted into the dibromide[23] and distilled. The fractions with boiling range of 104.7–105.0° at 16 mm. were treated with zinc in ethyl alcohol to regenerate the hydrocarbon; this was recovered by distillation of the reaction mixture, washing with successive portions of water, and drying with calcium chloride, yield 68%. Systematic fractionation through Column A gave a middle fraction with b. p. 72.63 ± 0.01° at 765 mm., f. p. −136.5°, n^{20}_{D} 1.3919.[24]

Tertiary Butylethylene.—A good grade of commercial *t*-butyl alcohol was distilled in Column C; a fraction boiling over 0.2° was used for the preparation of *t*-butyl chloride.[25] A sample of *t*-butyl chloride boiling flatly at 50.7° (766 mm.) (Column C) was used to prepare the Grignard reagent according to Whitmore.[26] Pure acetaldehyde, freshly distilled, was added to this reagent, the reaction mixture broken down and the product recovered in the usual manner. A 58% yield of pinacolyl alcohol was obtained based on *t*-butyl chloride used. This alcohol was converted, after fractionation, to the acetate by treatment with 10% excess acetyl chloride; the chloride was added slowly with stirring and the reaction mixture allowed to stand overnight. The excess acid chloride was then distilled off and the ester fractionated in Column B; a 61% yield was obtained, distilling at 80.5–80.9° at 99 mm.; n^{23}_{D} 1.4020 to n^{23}_{D} 1.4023.

Acetic acid was split out by a method suggested by Dr. Paul L. Cramer of General Motors (private communication), who obtained better yields than found in the original work of Whitmore and Rothrock.[27] Pinacolyl acetate was converted into *t*-butylethylene and acetic acid by passage through a reaction tube packed with glass wool in a furnace maintained electrically at 400°. The reaction product was washed free from acetic acid and the *t*-butylethylene separated from unchanged pinacolyl acetate by fractionation. The unchanged pinacolyl acetate was recovered nearly quantitatively and repassed through the

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(15) Cotton and Mouton, *Ann. chim.*, [8] **28**, 218 (1913), give $n^{20.8}_{\mathrm{D}}$ 1.5351.

(16) Boedtker, *J. pharm. chim.*, **15**, 225 (1932).

(17) Carothers and Adams, THIS JOURNAL, **45**, 1071 (1923).

(17a) Zelinsky and Lewina, *Ber.*, **66**, 477 (1933).

(18) Filipow, *J. Russ. Phys.-Chem. Soc.*, **46**, 1163 (1915) [*Chem. Zentr.*, **86**, I, 1057 (1915)], gives b. p. 44.1–44.6°; n^{18}_{D} 1.42183.

(19) Smith, Hurst and Read, *J. Chem. Soc.*, **123**, 1657 (1923), give the following constants for α-phellandrene from two different sources: b. p. 58–59° at 16 mm., n^{20}_{D} 1.4732; b. p. 62.5–63.5° at 15.5 mm., n^{20}_{D} 1.4744.

(20) Richter and Wolff, *Ber.*, **63**, 1720 (1930), give $n^{19.7}_{\mathrm{D}}$ 1.477.

(21) Richter and Wolff, *ibid.*, **63**, 1724 (1930), give $n^{17.2}_{\mathrm{D}}$ 1.4727 for *l*-limonene; this is probably the most recent figure.

(22) Norris and Reuter, THIS JOURNAL, **49**, 2624 (1927), give b. p. 20.10 ± 0.05° at 760 mm.; n^{15}_{D} 1.3675.

(23) Whitmore and Homeyer, *ibid.*, **55**, 4555 (1933).

(24) Whitmore and Homeyer[23] give b. p. 72.35° at 760 mm. and n^{20}_{D} 1.3911.

(25) "Organic Syntheses," Coll. Vol. I, p. 138.

(26) Whitmore and Badertscher, THIS JOURNAL, **55**, 1561 (1933).

(27) Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933).

furnace. The *t*-butylethylene thus obtained was then distilled from sodium and finally fractionated through Column A. The product used had the following physical constants: b. p. 41.18 ± 0.01° at 760 mm.; n^{20}_D 1.3765.[28]

2,4,4-Trimethylpentene-1 and 2,4,4-Trimethylpentene-2.—Technical diisobutylene was generously supplied us by Prof. George S. Parks of Stanford University. About 4 liters of this material was refluxed over sodium metal chips for one hour and then distilled. The resulting product, 2321 g., was fractionated in two distillations through Column A to give a rough separation of the two isomers. Each isomer was then carefully refractionated, giving the following data.

2,4,4-TRIMETHYLPENTENE-1[29] (LOW-BOILING ISOMER)
Charge 473 g., b. p. 101.51–.58°, 765 mm.

Fraction	B. p., °C. (765 mm.)	n^{20}_D	Wt., g.
DIB-27	101.22–.49	1.4075	110
DIB-28	101.49–.53	1.4082	60
DIB-29	101.53–.56	1.4087	77
DIB-30	101.56–.58	1.4089	122
DIB-31	101.58–.58	1.4089	28
Residues			46

2,4,4-TRIMETHYLPENTENE-2[29] (HIGH-BOILING ISOMER)
Charge 424 g. Residues from first fractionations

DIB-21	104.30–.74	1.4159	98
DIB-22	104.74–.84	1.4159	67
DIB-23	104.84–.83	1.4159	27
DIB-24	104.83–.85	1.4159	27
DIB-25	104.85–105.63	1.4160	80
DIB-26	105.63–106.56	1.4155	24
Residues			137

The structures of these isomers as assigned to them by Whitmore and Church[30] on the basis of ozonolysis were confirmed by the same method; we shall forego a discussion of the tedious details.

Pentadiene-1,3.—Crotonaldehyde from Carbide and Carbon Chemical Corporation was fractionated through Column B; the samples used distilled at 102.3–102.4° at 765 mm.

Methylmagnesium chloride Grignard reagent was made up in 5-molar lots in the usual way and crotonaldehyde, to which had been added about an equal volume of anhydrous ether, was added until a negative test for Grignard reagent was obtained with Michler's ketone. Grignard reagent from 25 moles of magnesium required 23.7 moles of crotonaldehyde. The reaction mixture was decomposed with water and an amount of 30% sulfuric acid added sufficient to neutralize the magnesium hydroxide formed. Upon working up the product, it was found to be not pentene-2-ol-4 but the ether from two moles of the pentenol as described by Baudringheim.[31]

The crude product was washed with saturated sodium bisulfite solution, and then water. The yield was 1290 g. (8.3 mole) corresponding to 70% based on crotonaldehyde. Fractionation in Column B gave 801 g. of product distilling at 158.5–158.9° at 770 mm., a yield of 44%.

The 801 g. of product was passed over freshly activated alumina for dehydration to pentadiene-1,3; better yields of olefin were obtained when the temperature of dehydration was 280–290°. The crude pentadiene was distilled through a three-foot (91-cm.) jacketed, indented column, giving 510 g. of material (72% yield) boiling at 35–45° and yielding a bromide upon saturating a small sample in carbon tetrachloride with bromine in the cold, that melted at 114–114.5°.[32] The once-distilled pentadiene was fractionated through Column B, giving 353 g. distilling at 41.2–42.6° at 770 mm. and this in turn was fractionated through Column A. Three samples totaling 70% of total charge were collected for use in the calorimeter:

Sample	B. p., °C. (760 mm.)[33]	n^{20}_D	F. p., °C.
P-2	41.85–.87	1.4304	−87.7
P-3	41.88–.90	1.4303	−88.1
P-4	41.91–.93	1.4304	−88.9

2,3-Dimethylbutadiene-1,3.—2,3-Dimethylbutadiene-1,3 was prepared by dehydrating pinacol over activated alumina.

The pinacol hydrate starting material was obtained from Professor L. F. Fieser of this Laboratory. To remove the water of hydration it was distilled at atmospheric pressure in Column C until the temperature of the distillate reached 122°. The residue from 3580 g. of hydrate amounted to 1475 g., a yield of 79%. The crude pinacol was subjected to distillation at 100 mm., giving 1226 g. (65% yield) of product; b. p. 117.4–117.5°; m. p. 43.2–43.4°.

Dehydration of the pinacol was accomplished by passing it through a tube 70 cm. long and 2.5 cm. in diameter filled with activated alumina at 450–500°. The product from 1179 g. of pinacol was distilled through Column B giving 585 g. (71.5% yield) of 2,3-dimethylbutadiene-1,3 distilling at 68.6–69.7° at 765 mm. This was fractionated through Column A; from 304 g. of olefin was obtained 153 g. distilling at 68.70 ± 0.01° at 765 mm.; f. p. −76.0° and n^{20}_D 1.4390.[34]

Data and Results

No important variations in calorimetric procedure have been adopted. With some of the higher boiling compounds, in order to obtain a workable rate of temperature rise, it was necessary to keep the device in which the hydrogen becomes saturated with the hydrocarbon at 100°; to ensure against condensation of reactant or product in the flow system, the operating temperature of the calorimeter was raised above the 82°

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[28] Schurman and Boord, THIS JOURNAL, **55**, 4930 (1933), give n^{20}_D 1.3759; Fomin and Sochanski, *Ber.*, **46**, 244 (1913), give n^{20}_D 1.37667; Laughlin, Nash and Whitmore, THIS JOURNAL, **56**, 1395 (1934), give n^{20}_D 1.3760.

[29] Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932), give for 2,4,4-trimethylpentene-1, b. p. 100.1 at 737 mm., n^{20}_D 1.4082, and for 2,4,4-trimethylpentene-2, b. p. 103.4 at 737 mm., n^{20}_D 1.4158.

[30] Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

[31] Baudringheim, *Bull. sci. acad. roy. Belg.*, **15**, 53 (1929).

[32] Beilstein, Vol. I, p. 132, gives 114.5° for 1,2,3,4-tetrabromopentane.

[33] Farmer and Warren, *J. Chem. Soc.*, 3224, (1931), report fractions of piperylene ranging in boiling point from 42.0–42.8° and in refractive index from n^{20}_D 1.4305 to 1.4314.

[34] Kogerman, *Naturforscher-Ges. Univ. Tartu*, **41**, Nr. 3/4 (1934), [*Chem. Zentr.*, **106**, I, 2965 (1935)], gives n^{20}_D 1.43929; b. p. 68.8–68.9° at 753.5 mm.

common to our earlier determinations. For purposes of comparison, all data have been reduced to 82° by use of ΔC_p values of −4 cal./deg. for addition of one H_2, −8 for $2H_2$, −12 for $3H_2$ and −16 for $4H_2$; errors resulting from this approximation are slight due to the small temperature ranges involved.[35]

Ethylbenzene + $3H_2$.—The table shows a high degree of precision, even with varied flow rates. The freezing point of the ethylbenzene was very sharp at −94.7°; addition of 0.5% benzene lowered the initial freezing point by 1.1° and the freezing curve dropped off steadily. A test for irreversible adsorption on the cobalt–nickel catalyst used was negative, as were tests designed to detect ethane and methane in the hydrogenated product. Unfortunately it proved impossible to freeze the product; even with prolonged chilling in liquid air the material remained glassy; n^{20}D 1.4333, to be compared with n^{20}D 1.4332[36] for ethylcyclohexane. We estimate the over-all accuracy of the determination as 100 cal./mole.

Run no.	Moles C_8H_{10}	Moles H_2 per min.	Moles C_8H_{10} per min.	$-\Delta H_{381}$ cal./mole
1	0.022190	0.0143	5.06 (10^{-4})	49,252
2	.022423	.0136	7.81 (10^{-4})	49,219
3	.022496	.0170	8.38 (10^{-4})	49,217
4	.022549	.0142	11.57 (10^{-4})	49,250
			Average	49,235 ± 17
			$-\Delta H_{355}$	48,920

o-**Xylene + $3H_2$.**—This hydrogenation over cobalt–nickel yields a mixture of isomers and no test of purity of the product by the freezing point method was possible; a glass resulted on chilling in Dry-Ice; n^{20}D 1.4321 to 1.4324.[37] The freezing "flat" of the *o*-xylene was not especially good, falling off 0.1° to 70% frozen material; however, addition of 0.5% of the lowest boiling fraction caused a freezing-point lowering of 0.2° and the curve fell off more rapidly than in the case of the pure material. Each run was tested chemically for completeness of hydrogenation by treating 1 cc. of the product with 7–10 small drops of concd. sulfuric acid for one and one-half minutes at 70°; blanks showed that 0.1% of *o*-xylene in the product caused the formation of a yellow tint. The test for irreversible adsorption was negative. The over-all accuracy is estimated at 200 cal./mole.

Run no.	Moles C_8H_{10}	Moles H_2 per min.	Moles C_8H_{10} per min.	$-\Delta H_{373}$ cal./mole
1	0.021830	0.01653	5.58 (10^{-4})	47,492
2	.021571	.01355	3.49 (10^{-4})	47,440
			Average	47,466 ± 26
			$-\Delta H_{355}$	47,250

Mesitylene + $3H_2$.—The freezing point of mesitylene was very sharp at −51.4°; addition of 0.8% benzene lowered the initial freezing point by 1.1° and the temperature dropped off steadily. A chemical test for completeness of reaction similar to that for *o*-xylene was used: 0.1% mesitylene in the product was detectable; all runs were complete. No freezing point of the hydrogenation product as a criterion of purity was possible, as a mixture of isomers results in this experiment; n^{20}D 1.4280.[38] Tests for the presence of methane in the effluent gases and for irreversible adsorption on the cobalt–nickel catalyst were both negative. The over-all accuracy is probably 200 cal./mole, which includes any uncertainty in the purity of the mesitylene. However, the average ΔH represents the formation of an unknown mixture of isomers and thus may have a not well-defined thermodynamic meaning. It would seem from the data of Eisenlohr and Gorr[38] that we are getting chiefly the *trans* isomer, but the agreement of the refractive indices may be fortuitous.

Run	Moles C_9H_{12}	Moles H_2 per min.	Moles C_9H_{12} per min.	$-\Delta H_{381}$ cal./mole
1	0.020505	0.0070	2.85 (10^{-4})	47,957
2	.020647	.0112	4.23 (10^{-4})	48,018
3	.020746	.0050	4.94 (10^{-4})	47,827
4	.011447	.0158	3.67 (10^{-4})	47,920
			Average	47,930 ± 57
			$-\Delta H_{355}$	47,620

Styrene + $4H_2$.—The data on this compound are quite consistent over a two-fold variation of hydrogen and styrene concentration. To ensure against polymerization the samples were stored in Dry-Ice and put into the clean saturating device just before the runs; this procedure was employed with all compounds for which polymerization was suspected. No methane or ethane was formed as concurrent side-reactions on the cobalt–nickel catalyst and no irreversible adsorption occurred. The styrene froze rather sharply at −30.5°; addition of 0.5% ethylbenzene lowered the initial freezing point by 0.2° and the "flat" was somewhat steeper. The hydrogenation product showed no definite freezing point, yielding a glass; n^{20}D 1.4333 (compare with product from ethylbenzene). The over-all accuracy is approximately 200 cal./mole.

Run	Sample	Moles C_8H_8	Moles H_2 per min.	Moles C_8H_8 per min.	$-\Delta H_{381}$ cal./mole
1	1	0.014153	0.0065	3.11 (10^{-4})	77,777
2	2	.013755	.0127	4.15 (10^{-4})	77,886
3	2	.013810	.0120	5.38 (10^{-4})	77,955
4	2	.013829	.0103	5.63 (10^{-4})	77,953
				Average	77,893 ± 61
				$-\Delta H_{355}$	77,480

Hydrindene + $3H_2$.—The tabulated data show fair consistency in the runs. The freezing point of the hydrindene was excellent at −51.4°; addition of 0.5% hydrogenation product lowered the initial freezing point by 0.3° and the temperature dropped off much more rapidly than with the pure material. A test for completeness of hydrogenation was devised: 1 cc. of the product + 10 small drops of concd. sulfuric acid at room temperature; blanks showed that as little as 0.1% of hydrindene in the product caused the formation of a definite brown color. The test was negative for all the reported runs, as was the test for ir-

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(35) A determination of the heat of hydrogenation of benzene to cyclohexane as a test of the calorimeter one year after the reported values (see IV) gave ΔH = −50,021 at 101.6°; corrected to 82° with ΔC_p = −12 cal./deg., ΔH = −49,788; this is to be compared with the earlier average of −49,802.

(36) Signaigo and Cramer, This Journal, **55**, 3331 (1933).

(37) "I. C. T.," Vol. I, p. 276, gives 1.430.

(38) Eisenlohr and Gorr, *Fortschr. Chem., Physik physik. Chem.*, **18**, H9 (1925), give *cis*-1,3,5-trimethylcyclohexane, n^{20}D 1.43010; *trans*-1,3,5-trimethylcyclohexane, n^{20}D 1.42710.

reversible adsorption on the cobalt–nickel catalyst. No freezing point of the product was possible as a mixture of stereoisomers is present; a glass resulted; $n^{20}\mathrm{D}$ 1.4688.[39] The over-all accuracy is approximately 250 cal./mole.

Run	Moles C_9H_{10}	Moles H_2 per min.	Moles C_9H_{10} per min.	$-\Delta H_{373}$ cal./mole.
1	0.022589	0.01217	5.01 (10^{-4})	46,061
2	.022652	.01486	4.89 (10^{-4})	45,867
3	.022490	.01482	4.64 (10^{-4})	46,055
4	.022652	.01519	5.12 (10^{-4})	45,966
			Average	45,987 ± 71
			$-\Delta H_{355}$	45,800

Indene + $4H_2$.

Run	Sample	Moles C_9H_8	Moles H_2 per min.	Moles C_9H_8 per min.	$-\Delta H_{373}$ cal./mole
1	3	0.014836	0.01356	3.48 (10^{-4})	70,096
2	3	.014877	.01597	3.82 (10^{-4})	70,089
3	4	.014768	.01691	3.16 (10^{-4})	70,342
4	4	.014965	.01830	4.35 (10^{-4})	69,829
5	4	.014711	.01601	2.92 (10^{-4})	70,448
6	3	.014541	.01568	2.16 (10^{-4})	70,390
				Average	70,199 ± 194
				$-\Delta H_{355}$	69,910

The table shows large variation in the calorimetric results. A plot of ΔH versus the reciprocal of the length of the run (or versus rate of flow of indene) shows an irregular increase of ΔH with increased contact time on the catalyst; however, the slowest run, 6, gives almost the same ΔH as the next two, Nos. 5 and 3. Incomplete reaction in the faster runs, as a possible explanation of this difficulty, must be ruled out for the following reasons. (1) Each run's product was tested for completeness by the sulfuric acid test used for hydrindene and gave negative results (blanks with indene proved the validity of the test). (2) The experimental molar refractivity, P, from the determined $n^{20}\mathrm{D}$ 1.4683 and d_{20} 0.8748 of the product from Run 3, is 39.46, and agrees well with the theoretical value, 39.37 calculated from Hückel's[40] figures for C_9H_{16}. (3) A comparison of the refractive indices of the product of "slow" Run 3 and of a non-calorimetric run faster than Run 4 was made by use of a Zeiss portable laboratory interferometer; this instrument had previously been calibrated with liquids of known index; the test showed the index of the product of the "fast" run only 0.00033 unit (23 scale divisions) higher than that of the "slow" run; this would correspond to about 0.3% incompleteness, while the maximum variation of the heats of hydrogenation is about 1%. (4) Comparison of the indices of the products from indene and hydrindene by means of the Zeiss interferometer shows that the latter is 0.00017 unit higher than the former. (5) Two cubic centimeters of the hydrogenation product from "slow" Run 3 in 30-cc. glacial acetic acid with 0.1 g. of platinum oxide and a trace of ferrous ion was treated in an Adams hydrogenation apparatus;[41] the test was negative as only the empirical amount of hydrogen for the catalyst was absorbed. Addition of 0.1 cc. of hydrindene resulted in the absorption of 60 cc. of hydrogen. This test for incompleteness was repeated with 4.4 cc. of product from a run faster than Run 4 and was likewise negative. Two cubic centimeters of indene was then hydrogenated in the Adams apparatus and approximately the theoretical amount of hydrogen was absorbed, corresponding to formation of octahydrindene.

In view of all this evidence we are completely puzzled and shall give only the over-all average ΔH. Compared with the fairly uniform data for hydrindene it seems entirely unlikely that varying amounts of the isomers of the hydrogenation product or that concurrent side-reactions, such as breakage of the five-membered ring, are causing the difficulty. As in the case of hydrindene, the hydrogenation product formed a glass and a freezing-point test of purity was impossible; $n^{20}\mathrm{D}$ 1.4683. The test for irreversible adsorption on the cobalt–nickel catalyst was negative. The freezing point of the pure indene was very sharp at −1.67°; an initial freezing-point lowering of 0.3° and a pronounced falling off in temperature resulted upon contamination of the indene with 0.5% hydrogenation product.

As a crude estimate of over-all accuracy we shall give 500 cal./mole.

Cyclopentene + H_2.—The freezing point of the cyclopentene was sharp at −134.6° and dropped off markedly on addition of 1% of hydrogenation product (initial f. p. −135.0°). The hydrogenation product froze at −93.4°,[42] 0.3° higher than that of the diene hydrogenation product (see IV, p. 151), but the trend of the freezing curve was the same as that of the diene. Each run was checked for completeness of hydrogenation by means of the bromine addition test (see II, p. 876). Tests for irreversible adsorption on the cobalt–nickel catalyst were negative; $n^{20}\mathrm{D}$ 1.4064.[43] The over-all accuracy is estimated as 60 cal./mole.

Run	Moles C_5H_8	Moles H_2 per min.	Moles C_5H_8 per min.	$-\Delta H_{355}$ cal./mole
1	0.038936	0.0094	9.93 (10^{-4})	26,921
2	.038939	.0117	9.94 (10^{-4})	26,905
3	.039062	.0085	14.01 (10^{-4})	26,920
4	.039121	.0127	14.19 (10^{-4})	26,915
			Average	26,915 ± 5

α-Phellandrene[44] + $2H_2$.—The data on the three related compounds, α-phellandrene, α-terpinene, and limonene, have no claim to high accuracy as we have such weak data regarding the purity of reactant and product. It probably is fair to assign a variation of 300 cal./mole to each final figure, as even fairly high percentages of other terpenes would not greatly influence the hydrogenation value.

This hydrogenation over cobalt–nickel yielded a product which was a mixture of isomers and formed a glass when chilled; $n^{20}\mathrm{D}$ 1.4376 to 1.4380.[45]

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[39] Hückel, Sachs, Yantschulewitsch and Nerdel, *Ann.*, **518**, 155 (1935), give for hydrindane (*cis*) $n^{20}\mathrm{D}$ 1.4713 to 1.4716.

[40] Hückel, "Theor. Grundlagen d. org. Chem.," Akad. Verlag., Leipzig, 2d ed., Vol. II, 1935, p. 86.

[41] We are indebted to Dr. E. B. Hershberg for his kindness in performing these experiments.

[42] "I. C. T.," Vol. I, p. 192, gives −93.3°.

[43] Compare with product from cyclopentadiene, $n^{20}\mathrm{D}$ 1.4065 (see IV); Landolt-Börnstein, Erg. IIb, p. 820, gives $n^{20}\mathrm{D}$ 1.40609 for cyclopentane.

[44] 2-Methyl-5-isopropylcyclohexadiene-1,3.

[45] "I. C. T.," Vol. I, p. 277, gives $n^{20}\mathrm{D}$ 1.437 for para-menthane; a vast variety of values may be found for this compound.

Run	Moles $C_{10}H_{16}$	Moles H_2 per min.	Moles $C_{10}H_{16}$ per min.	$-\Delta H_{381}$ cal./mole
1	0.018026	0.0115	5.88 (10^{-4})	53,625
2	.018017	.0096	5.88 (10^{-4})	53,619
			Average	53,622 ± 3
			$-\Delta H_{355}$	53,410

α-**Terpinene**[46] **+ $2H_2$.**—Each run was tested chemically for completeness of reaction. The product of this hydrogenation over cobalt–nickel formed a glass when cooled in liquid air; n^{20}_{D} 1.4403. We cannot explain the variation of the indices of the three hydrogenation products of these related compounds; it may be due both to varying amounts of impurity and to varying amounts of the isomers of *p*-menthane.

Run	Moles $C_{10}H_{16}$	Moles H_2 per min.	Moles $C_{10}H_{16}$ per min.	$-\Delta H_{355}$ cal./mole
1	0.014402	0.0158	3.50 (10^{-4})	50,717
2	.014409	.0158	3.26 (10^{-4})	50,694
			Average	50,705 ± 12

Limonene[47] **+ $2H_2$.**—A test for completeness of hydrogenation using concentrated sulfuric acid, similar to that developed for hydrindene, was applied to the product from each run; the efficiency of the test was proved with blanks. Irreversible adsorption on the cobalt–nickel catalyst was absent. A glass resulted when the product was chilled in liquid air; n^{20}_{D} 1.4389 to 1.4392.[48]

Run	Sample	Moles $C_{10}H_{16}$	Moles H_2 per min.	Moles $C_{10}H_{16}$ per min.	$-\Delta H_{373}$ cal./mole
1	3	0.019059	0.01433	3.79 (10^{-4})	54,239
2	4	.019084	.01552	3.61 (10^{-4})	54,242
3	2	.019143	.01739	5.15 (10^{-4})	54,295
				Average	54,259 ± 24
				$-\Delta H_{355}$	54,110

Isopropylethylene + H_2.—A controlled freezing point of the product was very satisfactory; the value was −159.6°;[49] $n^{14.5}_{\mathrm{D}}$ 1.3567.[50] Although a satisfactory freezing point suffices as a criterion of singleness of reaction, further independent test showed no degradation to lower hydrocarbons. The bromine test was used with all runs to indicate completeness. Irreversible adsorption on the 5% platinum-on-asbestos catalyst was absent. The over-all accuracy is 60 cal./mole.

Run	Moles C_5H_{10}	Moles H_2 per min.	Moles C_5H_{10} per min.	$-\Delta H_{355}$ cal./mole
1	0.035793	0.01160	8.73 (10^{-4})	30,366
2	.035977	.01000	10.56 (10^{-4})	30,324
3	.035968	.00912	9.28 (10^{-4})	30,322
4	.035800	.01230	7.49 (10^{-4})	30,331
			Average	30,336 ± 15

Neo-amylethylene + H_2.—The 4,4-dimethylpentene-1 had an initial freezing point of −136.5° and fell off to −136.8° at 80% frozen material; addition of 0.5% hydrogenation product lowered the initial freezing point to −136.9° and the rate of drift was faster than for the pure material. The hydrogenation product was very satisfactory, as evidenced by a sharp freezing point at −123.9°;[51] n^{20}_{D} 1.3823.[52] There was no irreversible adsorption on the cobalt–nickel catalyst. The bromine titration test was used to ensure completeness of reaction. 60 cal./mole may be given as the over-all accuracy.

Run	Moles C_7H_{14}	Moles H_2 per min.	Moles C_7H_{14} per min.	$-\Delta H_{355}$ cal./mole
1	0.035185	0.01258	5.81 (10^{-4})	29,525
2	.035618	.01314	11.42 (10^{-4})	29,538
3	.035405	.01307	7.89 (10^{-4})	29,533
			Average	29,532 ± 5

t-**Butylethylene + H_2.**—The freezing point determination of *t*-butylethylene was very unsatisfactory; even with carefully controlled cooling, the material would supercool, heat to an initial freezing point and the temperature would then gradually drop off at an almost linear rate. Even hydrocarbon subjected to two fractional recrystallizations in liquid air-baths behaved in this manner, and the initial freezing point was not appreciably changed. This material has been sent to Prof. Parks for his estimate of the situation.[52a] Likewise difficulty was experienced with the hydrogenation product: a glassy solid resulted even after many attempts. The test for irreversible adsorption on cobalt–nickel was negative, as were all the bromine addition tests for incompleteness of reaction; n^{20}_{D} product 1.3688.[53] We estimate the over-all accuracy as 150 cal./mole.

Run	Moles C_6H_{12}	Moles H_2 per min.	Moles C_6H_{12} per min.	$-\Delta H_{355}$ cal./mole
1	0.034537	0.01273	8.90 (10^{-4})	30,349
2	.034648	.00612	11.11 (10^{-4})	30,366
3	.034380	.01261	6.16 (10^{-4})	30,307
			Average	30,341 ± 22

2,4,4-Trimethylpentene-1 + H_2.—Parks, Todd and Shomate[54] have estimated the purity of this hydrocarbon, Sample DIB-30, as 99.5%. The hydrogenation product froze well at −107.4°;[55] n^{20}_{D} 1.3917.[56] All runs were complete as shown by the bromine titration method and the test for irreversible adsorption on cobalt–nickel was negative. The over-all accuracy is approximately 60 cal./mole.

Run	Sample DIB	Moles C_8H_{16}	Moles H_2 per min.	Moles C_8H_{16} per min.	$-\Delta H_{355}$ cal./mole
1	31	0.038412	0.00768	8.23 (10^{-4})	27,250
2	30 + 31	.038469	.01060	8.73 (10^{-4})	27,231
3	30 + 31	.038551	.00911	10.12 (10^{-4})	27,235
4	30	.038584	.01160	11.00 (10^{-4})	27,229
				Average	27,236 ± 7

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(46) 1-Methyl-4-isopropylcyclohexadiene-1,3.

(47) 1-Methyl-4-isopropenylcyclohexene-1.

(48) Compare with products from *α*-phellandrene and *α*-terpinene. All these materials should yield the same hydrogenation product.

(49) Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032 (1930), give −160.5° (112.6°K.) for 2-methylbutane.

(50) "I. C. T.," Vol. I, p. 193, gives m. p. −159.7°; p. 276 gives n^{20}_{D} 1.355 for 2-methylbutane.

(51) Parks, Huffman and Thomas, THIS JOURNAL, **52**, 3242 (1930), give −125.0° (148.1°K.) for freezing point of 2,2-dimethylpentane.

(52) Edgar and Calingaert, *ibid.*, **51**, 1540 (1929), give n^{20}_{D} 1.38233, f. p. −125.6°, for 2,2-dimethylpentane.

(52a) Prof. Parks informs us that his tests have been unavoidably delayed; they will be reported in one of his papers.

(53) Maman, *Compt. rend.*, **198**, 1323 (1934), gives n^{20}_{D} 1.37054 for 2,2-dimethylbutane. "I. C. T.," Vol. I, p. 276, gives n^{20}_{D} 1.369.

(54) Parks, Todd and Shomate, THIS JOURNAL, **58**, 2505 (1936).

(55) Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930), give −106.8° (165.3°K.) for 2,4,4-trimethylpentane; Bruun and Hicks-Bruun, *Bur. Standards J. Research*, **9**, 269 (1932), give −107.41°.

(56) Smyth and Stoops, THIS JOURNAL, **50**, 1883 (1928), give n^{20}_{D} 1.39163 for 2,4,4-trimethylpentane.

2,4,4-Trimethylpentene-2 + H_2.—Parks, Todd and Shomate[54] estimate the purity of this hydrocarbon, Samples DIB 23 + 24, as 98%; this lower purity was suspected by us in view of the distillation data (see Preparations). It seems likely that there exists another compound boiling only slightly above this isomer; this point is strongly supported by an examination of the distillation curves of Fenske, Quiggle and Tongberg.[57] The table shows that Run 1 on Sample DIB-25, from just above the "flat," gives a ΔH markedly different from those of Runs 2, 3 and 4 which are with Samples DIB-22 and -23 from the region of the "flat."[58]

Run	Sample	Moles C_8H_{16}	Moles H_2 per min.	Moles C_8H_{16} per min.	$-\Delta H_{355}$ cal./mole
1	DIB-25	0.037106	0.0112	7.97 (10^{-4})	28,232
2	DIB-22	.036906	.0098	7.48 (10^{-4})	28,398
3	DIB-22	.036952	.0116	8.79 (10^{-4})	28,398
4	DIB-23	.036963	.0137	9.10 (10^{-4})	28,379
				Average 2, 3, 4	28,392 ± 8

$n^{20}D$ of product: from 1, 1.3932; from 2, 3, 4, 1.3918.[59] The usual tests for completeness of reaction and for irreversible adsorption on the cobalt–nickel catalyst were negative. The initial freezing point of the hydrogenation product was −108.2° (compare with 2,4,4-trimethylpentene-1) and the freezing curve had a pronounced downward trend. This freezing-point depression and dropping-off shows that the impurity present is not the low-boiling isomer, which should yield the same saturated hydrocarbon upon hydrogenation, but rather some other material. In view of this evidence it is difficult to estimate the over-all accuracy of this determination.

Crawford and Parks[60] have determined the heat of hydrogenation of the mixture of diisobutylenes in the liquid phase; $\Delta H_{298} = -28,580$ (±800) cal./mole. Assuming with Fenske, Quiggle and Tongberg[57] that the pentene-1 is four times as abundant as the pentene-2, our data give for the heat of hydrogenation in gas phase of the mixed isomers at 298°K. $\Delta H = -27,240$. The agreement is fair, considering neglect of heats of vaporization.

Pentadiene-1,3 + $2H_2$.—The small amount of material available prevented an attempt to separate the *cis–trans* isomers of this diene. However, several hydrogenations over copper were made on the three main samples; these are listed in the table. The trend is the same as found with the butenes-2, suggesting that the *cis*-isomer is the higher boiling one. The various samples represent far from pure materials as the freezing points given are initial ones and in each case the curve fell off rapidly; addition of 0.5% pentane to Sample P-2 lowered the freezing point to −87.8° but the trend of the curve was essentially unaltered. However, 15 cc. of the hydrogenation product from several samples of the diene gave an excellent freezing "flat" at −129.6°,[61] showing conclusively that the starting material can only consist of 5-C straight-chain compounds. Thus it is fairly certain that the diene is a mixture of pure isomers, as presence of a mono-olefin is eliminated by the preparation. The bromine titration was used to show completeness of reaction; no degradation, polymerization or irreversible adsorption on the copper catalyst occurred. We have struck an average of all the ΔH values and present it as we did the value for the mixture of pentenes-2. The over-all accuracy is approximately 150 cal./mole.

Run	Sample	Moles C_5H_8	Moles H_2 per min.	Moles C_5H_8 per min.	$-\Delta H_{355}$ cal./mole
1	P-2	0.019887	0.0143	7.80 (10^{-4})	54,008
2	P-2	.019982	.0153	10.40 (10^{-4})	53,963
3	P-4	.019830	.0139	7.54 (10^{-4})	54,208
4	P-4	.019888	.0098	10.40 (10^{-4})	54,174
5	P-3	.019791	.0141	6.33 (10^{-4})	54,208
			Average for P-2		53,986 ± 23
			Average for P-4		54,191 ± 17
			Over-all average of runs		54,112 ± 101

2,3-Dimethylbutadiene-1,3 + $2H_2$.—The freezing point of the diene was sharp at −76.0° and addition of 0.5% hydrogenation product caused a lowering of 0.4°, although not much change in the freezing "flat" was noted. It proved impossible to freeze the hydrogenation product; a glass resulted in all attempts (contrast with results on products from *unsym*-methylisopropylethylene and tetramethylethylene; see III, p. 143); $n^{20}D$ product, 1.3748.[62] The bromine titration tests for completeness, tests for degradation to methane and for irreversible adsorption on the 5% platinum-on-asbestos catalyst were all negative. The over-all accuracy is approximately 150 cal./mole.

Run	Moles C_6H_{10}	Moles H_2 per min.	Moles C_6H_{10} per min.	$-\Delta H_{355}$ cal./mole
1	0.020092	0.0123	6.36 (10^{-4})	53,867
2	.020160	.0109	8.48 (10^{-4})	53,871
3	.020155	.0085	8.42 (10^{-4})	53,898
4	.020206	.0103	10.56 (10^{-4})	53,853
			Average	53,872 ± 13

Discussion

In order to conserve space we shall not attempt here a comparison of our data with those obtained by the combustion method. It is, however, noteworthy that in general combustion data on the more easily purified compounds agree much better with the present determinations than those made on difficult substances. This suggests that one of the major sources of error in those measurements is the inadequate purification of the materials.

With the three newly added monosubstituted ethylenes, isopropyl, neo-amyl and *t*-butyl ethylenes, the number of representatives of this group of hydrocarbons has been increased to six. It will be noted that with the exception of the neo-amyl group, the rest agree well among themselves,

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(57) Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

(58) Sample DIB-24 was not used in our calorimetric experiments as it was sent to Prof. Parks for his measurements.

(59) Compare with product from low-boiling isomer.

(60) Crawford and Parks, THIS JOURNAL, **58**, 373 (1936).

(61) Parks and Huffman, *ibid.*, **52**, 4381 (1930), give −129.7° (143.4°K.) for *n*-pentane.

(62) Compare with indices of product from *unsym*-methylisopropylethylene, $n^{20}D$ 1.3746; product from tetramethylethylene, $n^{20}D$ 1.3747 (omitted from III); "I. C. T.," Vol. I, p. 276, gives $n^{20}D$ 1.3783 for 2,3-dimethylbutane.

averaging 30,200 ± 100 cal./mole. The neo-amyl group, however, gives a distinctly lower result but the suggestion in paper III that branched-chain substituents are generally more effective in lowering the heat of hydrogenation can no longer be supported. Instead it must be concluded that introduction of branched-chains near the double bond leads to heats of hydrogenation which cannot be so accurately represented by the simple rules postulated in paper III as is possible with straight-chain alkyls. This is shown very clearly by the isomeric diisobutylenes. The lower boiling, 2,4,4-trimethylpentene-1, agrees still quite well with predictions. Its heat of hydrogenation is some 800 to 1000 cal. lower than those of other unsymmetrical disubstituted ethylenes (see III), whereas neo-amylethylene has a value which is lower by 600 to 800 cal. than those of other monosubstituted compounds. The 2,4,4-trimethylpentene-2, however, is completely anomalous. The same rules would predict for it a value of some 27,000 cal. (as in trimethylethylene) and in any case a value lower than that of its isomer. Instead, 28,400 cal. is found. Two per cent. impurity found by Parks, Todd and Shomate[54] does not explain the discrepancy unless the impurity is supposed to be a diene, perhaps C_7H_{12}, formed by splitting out of methane in the process of manufacture, boiling at nearly the same temperature. This is admittedly not very probable, but the structure of this hydrocarbon has been determined reliably by ozonolysis. Because of the good applicability of the hydrogenation rules as tested heretofore with pure compounds of established structure the possibility of diene impurity cannot be ignored.

However, Samples DIB-23 and 24 were returned to us by Professor Parks for further tests. At his suggestion we tested for peroxides by means of potassium iodide–starch solutions with negative results. Also, thirty-two grams of this material was treated with 0.65 g. of maleic anhydride on a steam-bath at 50° for thirty minutes; the diisobutylene was distilled off under reduced pressure at 35°, washed with potassium carbonate solution and dried with potassium carbonate. It was then subjected to a fractional distillation in a small Podbielniak-type column at a 10:1 reflux ratio; from 30 g. of material there was obtained 25 g. boiling at 104.8° (760 mm.). A calorimetric run was made on this sample and its heat of hydrogenation found to be −28,337 cal./mole. Thus it seems that, if the discrepancy regarding this compound is to be attributed to a diene impurity, at least the diene present cannot be a conjugated one, capable of reacting with maleic anhydride.

With substituted conjugated dienes the introduction of alkyl groups also results in a lowering of the heat of hydrogenation, but the regularities are not very clear cut. Thus the change from butadiene to cyclohexadiene (equivalent to substitution on both ends of the chain) (see IV) lowers the heat by 1700 cal., butadiene to 1-methylbutadiene-1, 3 results in 3000 cal. change, and an introduction of two methyl groups in 2,3-positions causes 3100 cal. lowering. These apparent irregularities are probably connected with small changes of the conjugation resonance energy. If one assumes that precisely the same rules hold for substitution of alkyls in dienes as do in mono-olefins the resonance energies are found to vary from 4000 to 1800 cal.

The study of the terpenes was undertaken chiefly to verify the data on cyclohexadiene-1,3 in view of the importance of this compound in the light of a considerable disagreement with the older thermochemical data. The new results confirm the heat of hydrogenation of cyclohexadiene as well as can be expected considering the somewhat uncertain state of purity of the new substances. In α-phellandrene one of the double bonds receives an additional methyl substituent as compared with cyclohexadiene. Taking for this effect the value of 1500 cal. (difference between butene-2-*cis* and trimethylethylene), we calculate 53,800; obsd. 53,400. α-Terpinene has two new substituents on both double bonds; hence its heat of hydrogenation according to the same rule should be 52,300 whereas 50,700 is found. Limonene is not conjugated; to calculate its heat of hydrogenation we take the figure for methylisopropylethylene (28,000) and add to it monosubstituted cyclohexene (27,100) obtaining 55,100; found 54,100 for $-\Delta H$. Roth[62a] has stated, on the basis of the heats of combustion of α-phellandrene (1435 Cal.) and 1,3-dimethyl-5-ethenecyclohexene-3 (1455 Cal.), that a shift of a double bond from a side chain into the ring in a conjugated position liberates *ca.* 20 Cal. Our values for α-phellandrene and limonene do not confirm this. The discrepancy may well be attrib-

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(62a) Roth, *Z. Elektrochem.*, **17**, 789 (1911).

uted to the purity of the compounds used in the combustion measurements.

Benzene derivatives show a general lowering of their heats of hydrogenation as compared with parent substance. The lowering is rather small, being 900, 1300 and 700 cal. per substituent group in ethylbenzene, *o*-xylene and mesitylene, respectively. These figures are distinctly lower than those for the third substituent in aliphatic compounds, but the trend is in general the same. It is to be noted that the substituents on the benzene ring have little effect on the resonance energy. The heat of hydrogenation of the ethylenic group in styrene can be calculated readily by comparison with ethylbenzene and is found to be 28,560 cal. It is noteworthy that the conjugation energy with the benzene ring is quite small, amounting to only 1600 cal. This is a case where the use of thermochemical data has led to quite different results.[63] The heat of combustion, however, undoubtedly was falsified by the presence of polymerized material, which fortunately does not affect the present method as the high-boiling polymer is not carried by the passing gas stream into the calorimeter.

We now come to compounds containing five-membered carbon rings and it is desirable to consider them from a unified point of view. In paper IV the heat of hydrogenation of cyclopentadiene was reported as 50,865 cal., which is 4500 cal. lower than that of cyclohexadiene-1,3. This was interpreted as due to increased resonance energy but present measurements do not bear out this point of view. Indeed the heat of hydrogenation of cyclopentene, 26,915 cal., is 1680 cal. lower than that of cyclohexene and thus the resonance energies in the two cases are practically the same. The uniformly lower values in the five-membered ring systems, however, are very puzzling. If it is assumed tentatively that the entire difference between the six- and the five-membered series is due to strain and that the six-membered rings, whether saturated or unsaturated, are practically strainless,[64] then it follows that with increasing saturation of the five-membered rings the strain increases. Namely, to explain the lowered heat of hydrogenation one must suppose that in the process of hydrogenation part of the available energy is retained by the molecule as increased strain instead of being liberated as heat.

The reliability of these experimental findings receives independent support from the study of indene and hydrindene. Unfortunately at present there are no values of 1,2-dihydronaphthalene[65] to be compared with indene but we may use the data on styrene and correct them for substitution according to the rules previously developed. Correcting for orthosubstitution on the benzene ring of styrene (difference between ethylbenzene and *o*-xylene) and for second substitution on the side chain double bond, we arrive at 73,700 cal. The observed value for indene is 69,900 and while both may be rather considerably in error, the magnitude of the difference is much too large to be explained away on this basis.

Quite similar are the results obtained with hydrindene. It may be compared directly to *o*-xylene because, as we have found earlier, the change from methyl to longer chain radicals does not affect appreciably the heat of hydrogenation. Hence, if the five-membered ring acts in all respects as an aliphatic chain the two figures should be identical. Actually it is found that hydrindene has a 1400-cal. lower heat of hydrogenation. For the logical validity of this comparison it is not necessary to fix the double bonds in the benzene ring. The physical facts are that after hydrogenation we have a five-membered saturated (substituted) ring and that in the process of hydrogenation this system has been obtained from one which lacked two hydrogens in adjacent positions common to the benzene ring. By comparison with *o*-xylene we note that the introduction of these two hydrogens into the five-membered ring releases less heat than a similar process when the ring is not closed as in *o*-xylene. (We are supposing here that the other hydrogenated positions in the benzene ring are less affected by the five-membered ring than these particular two atoms; for this we have complete justification from all data on the heats of hydrogenation.)

It is seen thus that indene and hydrindene fall in line with cyclopentadiene and cyclopentene, namely, there is less heat evolution when these compounds take up hydrogen and become

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[63] Pauling and Sherman, *J. Chem. Phys.*, **1**, 684 (1933), give 6900 cal. (calcd.); 6700 (obsd.).

[64] Cyclohexane and cyclohexene are entirely strainless on the basis of the tetrahedral carbon atom model if one allows non-planar rings. Cyclohexadiene, even when planar, is under a very slight strain, when accepted internuclear distances are used. Perhaps this explains the slightly lower magnitude of the resonance energy found by us for cyclohexadiene as compared with other conjugated dienes.

[65] Data on this and related compounds may soon be available from determinations of heats of hydrogenation in the liquid phase made by Dr. R. B. Williams of this Laboratory.

saturated five-membered rings than when the corresponding process occurs in open chains or six-membered rings.

The data on cyclopentene and cyclopentadiene can be summarized by stating that the former has a strain smaller by some 1600 cal. and the latter one smaller by *ca.* 4000 cal. than cyclopentane. And since the latter, as combustion data[66] indicate, is itself under a strain of about 4000-5000 cal., there appears to be no strain in cyclopentadiene and a very small one in cyclopentene.

These facts are quite difficult to reconcile with tetrahedral angle carbon atom models. Construction of diagrams of the five-membered rings readily shows that the strain in these rapidly increases with increasing unsaturation. The use of 1.53 Å. for the single bond and 1.36 Å. for the double bond distances, together with tetrahedral angles, reveals that in cyclopentane the formation of the planar pentagon produces a strain due to the closure of a gap of 0.16 Å. In cyclopentene the gap has increased to 1.34 Å. and in cyclopentadiene it is 2.06 Å. In this last case the gap is hardly larger than in the model of cyclobutane, which latter compound, as it is known, is under a severe strain. Indeed, on studying these models, one wonders how cyclopentadiene, if it has this theoretical stereochemical structure, could ever have been found in the distillation of coal.

The discrepancy can be, of course, formally ascribed to some other, as yet unstudied, competing effects which overshadow the strains. Such an attitude, however, is very unsatisfactory since the strain theory itself was introduced to explain the instability of certain atomic configurations in organic compounds and one rather must conclude that the magnitude of strains cannot be evaluated in some special cases, at least, on the basis of the tetrahedral angle model. The problem is one of great interest and further work on small, unsaturated rings, in particular on lactones and acid anhydrides, is planned.

Some comments concerning the fixation of double bonds in benzene rings are in order. From the conclusions as to the relative strains in the five-membered rings one cannot, of course, arrive at definite conclusions about the positions of double bonds in the attached benzene ring. One point is quite clear, however, if in the tetralin molecule the saturated ring does not prevent the free resonance between the two Kekulé formulas, in hydrindene such resonance cannot be hindered in favor of a single bond being made a part of the five-membered ring. This is evident because more heat is evolved when an unsaturated six-membered ring is converted into a saturated one than when this happens to a five-membered ring. The entropies of the two processes are unknown but one might surmise, with a considerable degree of certainty, that they are not far different from one another. Hence there will be less driving force for the five-membered ring in hydrindene to become saturated than for the six-membered one in tetralin. This is in decided disagreement with conclusions reached by Mills and Nixon,[67] Sidgwick and Springall[68] and Fieser and Lothrop[69] from their studies of other phenomena. As these phenomena are rather complex it is somewhat questionable whether their conclusions are the only plausible ones.

Acknowledgment.—It is a pleasant duty to thank Prof. E. P. Kohler and Dr. J. B. Conant for many helpful suggestions and criticisms which have aided materially the progress of this work, which was made possible by a grant from the Rockefeller Foundation.

ERRATA AND ADDENDA

(1) In III, p. 143, there should be recorded the n^{20}D of the product from tetramethylethylene = 1.3747.

(2) In IV, p. 150, 5% Pt-on-asbestos was the catalyst used in the hydrogenation of cyclopentadiene.

(3) Parks, Todd and Shomate[54] have given the following estimates of purity: in III, heptene-1, 99.85%; in III, tetramethylethylene, "probably of similar high order"; in IV, 1,4-pentadiene, 99.90%.

Summary

The heats of hydrogenation of the following substances have been determined:

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[66] Hückel, "Theor. Grundlagen d. org. Chem." Akad. Verlag., Leipzig 2d ed., Vol. I, 1935, p. 60, gives 5000 cal. Consistent use of Swietoslawski's data on cyclopentane and cyclohexane [as given by Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929)] and Rossini's very reliable data on the straight-chain compounds [*ibid.*, **13**, 21 (1934)] corrected from gas to liquid state, gives −13,200 and −9700 as the heats of formation of the straight-chain compounds from the cyclic ones; the strain in cyclopentane is thus 3500 cal.

[67] Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

[68] Sidgwick and Springall, *Chemistry and Industry*, **55**, 476 (1936).

[69] Fieser and Lothrop, THIS JOURNAL, **58**, 2050 (1936).

Substance + xH_2	°K.	ΔH, cal./mole	Deviation, cal.	Over-all accuracy, cal.	$\Delta H_{355°}$ 82° C., cal./mole
Ethylbenzene + $3H_2$	381	−49,235	±17	±100	−48,920
o-Xylene + $3H_2$	373	−47,466	±26	±200	−47,250
Mesitylene + $3H_2$	381	−47,930	±57	±200	−47,620
Styrene + $4H_2$	381	−77,893	±61	±200	−77,480
Hydrindene + $3H_2$	373	−45,987	±71	±250	−45,800
Indene + $4H_2$	373	−70,199	±194	±500	−69,910
Cyclopentene + $1H_2$	355	−26,915	±5	±60	−26,915
α-Phellandrene + $2H_2$	381	−53,622	±3	±300	−53,410
α-Terpinene + $2H_2$	355	−50,705	±12	±300	−50,705
Limonene + $2H_2$	373	−54,259	±24	±300	−54,110
Isopropylethylene + $1H_2$	355	−30,336	±15	±60	−30,336
Neo-amylethylene + $1H_2$	355	−29,532	±5	±60	−29,532
t-Butylethylene + $1H_2$	355	−30,341	±22	±150	−30,341
2,4,4-Trimethylpentene-1 + $1H_2$	355	−27,236	±7	±60	−27,236
2,4,4-Trimethylpentene-2 + $1H_2$	355	−28,392	±8	?	−28,392
Pentadiene-1,3 + $2H_2$	355	−54,112	±101	±150	−54,112
2,3-Dimethylbutadiene-1,3 + $2H_2$	355	−53,872	±13	±150	−53,872

1. The previously discussed rules correlating the heat of hydrogenation with the structure of unsaturated hydrocarbons have been extended. It has been found that branched-chain substituents do not follow the rules as well as do the straight chains.
2. The evidence of the heats of hydrogenation of the five-membered carbon ring systems points to a strain which decreases as unsaturation increases. This is quite contrary to conclusions which may be drawn from tetrahedral angle carbon atom models. The implications of these results are discussed.

CAMBRIDGE, MASS.

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

Dibenzylideneglucose and Dibenzylideneglucuronic Acid from 6-Benzoyldiethylmercaptoglucose. Synthesis of Another Dibenzylideneglucose from 4,6-Benzylideneglucose

BY PHILIPPOS E. PAPADAKIS

It is known that acetals of aromatic aldehydes and sugars are obtainable in pure crystalline form. Benzylidene derivatives of sugars which have part of their hydroxyl groups blocked are convenient starting materials in synthetic work.[1] The application of catalytic hydrogenation to such acetals of aromatic aldehydes and sugars for the splitting of the benzylidene residue, wherever the acid hydrolysis is objectionable, constitutes another advantage in favor of their use.

The present author had occasion in the past to prepare 6-benzoyldiethylmercaptoglucose in pyridine solution at 0°. This was used as a starting material for the preparation of a dibenzylidene derivative of glucose. The method adopted was similar to that used by L. Zervas[1] in the preparation of 4,6-benzylideneglucose. In the course of the experimental work it was found that the ethyl mercaptal groups were split off and a monobenzoyl dibenzylidene derivative of glucose resulted which does not reduce Fehling's solution. It is thought that the compound may be 1,2,3,5-dibenzylidene-6-benzoyl-*α*-*d*-glucofuranose. If that be the case then by hydrolyzing the benzoyl group one may obtain 1,2,3,5-dibenzylidene-*α*-*d*-glucofuranose. The latter by subsequent oxidation should yield 1,2,3,5-dibenzylideneglucuronic acid which could be changed into glucuronic acid. The benzoyl residue of the monobenzoyldibenzylideneglucose was split off by means of either alcoholic potassium hydroxide solution and heat or by means of the calculated amount of sodium methoxide in chloroform at 0°. The resulting

[1] L. Zervas, *Ber.*, **64**, 2289 (1931); P. Brigl and R. Schinle, *ibid.*, **66**, 325–30 (1933); P. Brigl and H. Grüner, *ibid.*, **65**, 1428 (1932); P. Brigl and O. Widmaier, *ibid.*, **69**, 1219 (1936); P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **53**, 431 (1922); *ibid.*, **57**, 319 (1923).

dibenzylideneglucose does not reduce Fehling's solution. On oxidation it yielded dibenzylideneglucuronic acid, m. p. 175°. The oxidation under the conditions of the experiment described later was difficult because of the low solubility of the substance in the presence of water. Attempts to oxidize the substance with alkaline permanganate in acetone–water solution or in dioxane were given up temporarily because the permanganate was reduced by the solvents.

At this point it was thought that if part of the benzoylmercaptoglucose had its benzoyl group located on some other carbon than the sixth, then the benzylidene group would block carbon no. 6 and the resulting monobenzoyldibenzilideneglucose would not oxidize. Since Zervas obtained a 4,6-monobenzylideneglucose by treating glucose in the benzaldehyde with zinc chloride, it seemed plausible that if the hydroxyls of carbons 4 and 6 of the monobenzoylmercaptoglucose were free, then when the latter is treated with benzaldehyde and anhydrous zinc chloride the benzaldehyde group may go into acetal formation with them. In that case a 3-benzoyl-1,2,4,6-dibenzylideneglucose would be a possibility and hence a 1,2,4,6-dibenzylideneglucose would result from the hydrolysis of the benzoyl group. Zervas' work on 4,6-benzylideneglucose[1] and on 1,2-acetone-5,6-benzylidene-*α*-*d*-glucofuranose[2] suggests that by treating 4,6-benzylideneglucose with benzaldehyde in the presence of phosphorus pentoxide, one may obtain a 1,2,4,6-dibenzylideneglucose. As is shown later, a dibenzylideneglucose derivative was obtained by this method, m. p. 163°. Mixed melting points with this substance were tried with dibenzylideneglucose from the mercaptoglucose method before the oxidation to dibenzylideneglucuronic acid, and with the residue which had not oxidized. In both cases the melting point was depressed to the same extent. Further work is contemplated for the elucidation of the structure of these compounds.

Experimental

6-Benzoyldiethylmercaptoglucose.—The method used for the preparation of 6-benzoyldiethylmercaptoglucose is essentially the same as that of Lieser and Schweitzer[3] with some modifications.

Benzoyl chloride (1 mole) was added slowly with stirring to a saturated solution of diethylmercaptoglucose (1 mole) and anhydrous pyridine. The latter was cooled previously to 0°. The reaction mixture was kept at 0° for three hours; then the pyridine was extracted with petroleum ether and the residue was poured into ice water. Crystals of monobenzoyldiethylmercaptoglucose, m. p. 112°, were separated, washed with water, filtered and recrystallized by dissolving the crystals in boiling methanol and then cooling the solution to 0°. The compound melted at 114°; $[\alpha]^{23}\text{D} + 47.23°$ (0.4393 g. in 25 cc. of chloroform solution in a 1-dm. tube rotates 0.83° to the right). Lieser and Schweizer did not give specific rotation while Brigl and Grüner[3] reported m. p. 111–112° and $[\alpha]\text{D} + 45.82°$.

Anal. Calcd. for $C_{17}H_{26}O_6S_2$: C, 52.30; H, 6.66. Found: C, 52.23; H, 6.70.

The 6-benzoyldiethylmercaptoglucose prepared as above was dissolved in pyridine and boiled under a reflux condenser for three hours. Afterward it was reclaimed from pyridine and recrystallized as above. The specific rotation did not change.

6-Benzoyldibenzylideneglucose.—Anhydrous zinc chloride (6.5 g.) was added in small portions with shaking to a mixture of 4.9 g. of 6-benzoyldiethylmercaptoglucose and 30 cc. of benzaldehyde. The bottle containing the reaction mixture was kept in an ice-bath during the mixing period and later was placed on a shaking machine for fifteen minutes. The resulting solution was allowed to stand at room temperature for two hours. The benzaldehyde was extracted with petroleum ether and the glucose derivative with ethyl acetate. The latter solution was shaken with a saturated solution of sodium chloride and separated. From the ethyl acetate solution 2.2 g. of 6-benzoyldibenzylideneglucose, m. p. 156°, was obtained. It does not reduce Fehling's solution.

Anal. Calcd. for $C_{27}H_{24}O_7$: C, 70.40; H, 5.25. Found: C, 70.35; H, 5.21.

Dibenzylideneglucose.—6-Benzoyldibenzylideneglucose (2.5 g.) was boiled for three hours under a reflux condenser with an alcoholic solution of potassium hydroxide (1 g.). Then the solution was diluted to five times its volume with water. The crystals separating melted at 161°. They were recrystallized from ether and then from methanol, m. p. 163°; yield 1.5 g.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.38; H, 5.66. Found: C, 67.07; H, 5.49. Calcd. for $C_{20}H_{20}O_6$: C, 67.38; H, 5.66. Found: C, 66.97; H, 5.68.

Dibenzylideneglucuronic Acid.—Twenty-five cc. of 2 *N* sodium hydroxide and 0.5 cc. of bromine were added with shaking to a solution of 1.4 g. of dibenzylideneglucose (m. p. 161°) and 20 cc. of pyridine at 0°. After five minutes the reaction mixture was placed on a shaking machine for fifteen hours. Only part of the substance dissolved and the remaining material was filtered off. The filtrate was cooled to 0° and titrated with concd. hydrochloric acid until Congo red paper changed to blue. Needle-like crystals were formed which were dissolved immediately in ethyl acetate. The ethyl acetate solution was shaken with potassium bicarbonate solution until it showed an alkaline reaction and was then separated from the water solution. The latter was cooled to 0° and titrated with concd. hydrochloric acid as before. The crystals were filtered off, redissolved in potassium bicarbonate, the solution cooled and

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(2) L. Zervas and P. Sessler, *Ber.*, **66**, 1328 (1933).

(3) P. Brigl and H. Grüner, *Ann.*, **495**, 60–83 (1932); Th. Lieser and Richard Schweitzer, *ibid.*, **519**, 271–278 (1935).

retitrated as before. This process was repeated three more times; 200 mg. of crystals was obtained. They were dissolved in alcohol and reprecipitated with distilled water, m. p. 175°.

Anal. Calcd. for $C_{20}H_{18}O_7$: C, 64.83; H, 4.9. Found: C, 64.93; H, 5.08.

Dibenzylideneglucose from 4,6-Benzylideneglucose.—4,6-Benzylideneglucose (2.1 g.) previously dried over phosphorus pentoxide was mixed with phosphorus pentoxide (2 g.) in a dry Erlenmeyer flask. All precautions were taken to avoid moisture. To this mixture was added freshly distilled benzaldehyde (7 cc.), previously cooled to 0°. The reaction flask was stoppered quickly and shaken in an ice-water-bath for ten minutes. Then it was taken out of the ice-bath and shaken twenty minutes at room temperature. Dry ether was added to extract the substance and the ether solution was washed with saturated sodium chloride solution made alkaline with a little ammonium hydroxide. The ether layer was separated and, after partially evaporating the ether, petroleum ether was added. The crystals formed were separated, boiled with water, filtered off from the hot water and then recrystallized from ether and finally from methanol, m. p. 163°. It does not reduce Fehling's solution. Mixed melting points of this substance were tried (a) with dibenzylideneglucose from the mercaptoglucose method before the oxidation to dibenzylideneglucuronic acid, m. p. 143–148°, and (b) with the residue which had not oxidized, m. p. 142–148°; mixed melting points of dibenzylideneglucose from (a) with residue from (b), m. p. 163°.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.38; H, 5.66. Found: C, 67.39; H, 5.92.

The author wishes to express his appreciation to Dr. L. Zervas for the interest which he has shown in this work, and to Mr. D. Rigakos of the Rockefeller Institute for Medical Research for the microanalyses for carbon and hydrogen.

Summary

1. 6-Monobenzoyldibenzylideneglucose was prepared by treating 6-monobenzoyldiethylmercaptoglucose with benzaldehyde and anhydrous zinc chloride. It does not reduce Fehling's solution.

2. Dibenzylideneglucose was prepared from 6-monobenzoyldibenzylideneglucose. The compound does not reduce Fehling's solution.

3. Dibenzylidene glucose was oxidized to dibenzylideneglucuronic acid.

4. Dibenzylideneglucose was prepared from 4,6-benzylideneglucose. It does not reduce Fehling's solution. It was found to differ from the dibenzylideneglucose prepared from 6-benzoyldiethylmercaptoglucose.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

On 1,2- and 1,4-Addition.[1] II. Nitrogen Tetroxide and Trimethylethylene

BY ARTHUR MICHAEL AND G. H. CARLSON

Probably no other reagents act so diversely upon ethylenic hydrocarbons as the higher oxides of nitrogen and the reactions, although repeatedly investigated, are still understood very incompletely. The relative negativity of the possible addenda components, formed by intramolecular fission of nitrogen tetroxide, should decrease in the order. $ONO_2 > ONO > NO_2 > NO$ and, correspondingly, the polarity differences between the paired addendum groups of the following combinations should decrease as follows: $ONO_2 + NO > ONO + NO_2$. Alkenes in which the polarities of the Δ-carbons differ considerably should, therefore, add the tetroxide to form the nitroso-nitrate and less of the nitro-nitrite. This relationship has not been realized experimentally with alkylenes owing, largely, to the protean chemical character of the addendum. It may function not only as the balanced system $2NO \rightleftarrows O_2N—O—NO$, but as a powerful oxidant upon the alkene; further, as a polymerizing reagent upon alkenes easily susceptible to that process and the polymers may be reacted upon by the tetroxide.

Schmidt[2] passed the gas formed by heating lead nitrate into a cooled, ether solution of trimethylethylene until "saturated" and obtained mainly a greenish-blue oil with a varying yield (maximum 25%) of crystalline trimethylethylene nitrosate.[3] This compound was shown

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[1] For a previous paper in this series see, THIS JOURNAL, **59**, 744 (1937).

[2] Schmidt, *Ber.*, **35**, 2336 (1902). Guthrie [*J. Chem. Soc.*, **13**, 35, 129 (1861)] by the action of nitric acid, or of nitrogen tetroxide, upon trimethylethylene obtained, besides unidentified oily products, a colorless crystalline compound $C_5H_{10}N_2O_4$. This substance was prepared by Wallach [*Ann.*, **262**, 324 (1891)] by the action of nitric acid upon a solution of the alkene and isoamyl nitrite in acetic acid. From its chemical behavior, Wallach concluded the product is $C_5H_{10}(NO)(ONO_2)$ or $C_5H_9(=NOH)(ONO_2)$.

[3] The strongly oxidative, undried gas was used in a large excess and the solution stood at room temperature for a long time. Besides oxygen, nitrous and nitric acids were introduced into the reaction

TABLE I

Expt. no.		I	II	III	IV	V	VI	VII	VIII
Tetroxide, g.		18.8	19.4	22.2	19.8	11.0	21.0	8.0	2.4
Amylene	g.	20.0	25.0	25.0	20.0	12.0	22.0	20.0	8.0
Excess	%	40.0	69.0	48.0	32.0	43.0	37.5	230	340
Solvent, cc.	Ether	150	75	100			No solv.	No solv.	Gas phase
	Petrol				150	100			
Temp., °C.		−15	−15	−2	−15	0	−7	−80	30
Time of addition, min.		60	60	180	60	330	90	120	120
Product, g.	Solid	0.05	2.1	3.2	12.3	7.6	18.1	6.1	2.0
	Liquid	36.3	35.0	39.0	21.0	12.0	18.7	8.0	1.2
	Total	36.35	37.1	42.2	33.3	19.6	36.8	14.1	3.2
	Calcd.	33.2	34.2	39.2	34.9	19.4	37.0	14.1	4.2
Nitrosate, %		0.15	6.2	8.2	35.2	39.2	49.0	43.2	47.6

by Schmidt to be dimeric in a cold, colorless solution, but to dissociate appreciably, at 30°, into the blue, monomeric form. When fused, the bis-nitrosate, in contrast to the bis-nitrosite,[4] could not be depolymerized, but completely decomposed; accordingly, only in a dilute solution is there any indication of the existence of the monomeric form. Yet, Schmidt concluded that the main reaction product, the greenish-blue oil, principally because of its color and because a small amount of the bis-nitrosate gradually separated from the oil, consisted, mainly, of the monomeric trimethylethylene nitrosate, notwithstanding that the oil could not be purified, did not analyse correctly, became discolored and decomposed on standing.

Schmidt believed that the polymerization of the mono- to the bis-nitrosate was a slow process, but Klingstedt[5] noticed that the separation of the bis-nitrosate was complete after two to four hours and concluded that the blue oil is not the monomeric nitrosate. In support of this view, he showed that the bis-nitrosate with aniline gave trimethylethylene nitrolamine, whereas the blue oil gave undefined products.

Previous work[2,6] has shown that reduction with metals, in acidic, basic or neutral media, is generally not a satisfactory method for establishing the structure of the nitrogen tetroxide addition products. Catalytic reduction, too, under varied conditions, gave us indefinite results; ammonia was formed invariably and amines were isolated in yields too low to permit of identification. Since potassium thiophenylate reacts with benzyl nitrate and yields potassium nitrate and benzyl phenyl sulfide quantitatively,[7] it seemed probable that the mercaptide might be used to characterize ester groups formed in the addition of nitrogen tetroxide to alkenes. Sodium thiophenylate and the ethyl mercaptide replace, quantitatively, the nitric ester radical in bis-trimethylethylene nitrosate to yield the corresponding thio ethers

$$[CH_3CH(NO)C(ONO_2)(CH_3)_2]_2 + 2RSNa \longrightarrow 2CH_3CH(NO)C(SR)(CH_3)_2 + 2NaNO_3$$

The thio ethers gave colorless solutions in hot benzene, but were partially associated in the freezing solvent, in this respect behaving like β-triazo-β-methylbutan-γ-oxime.[8] The thio ethers unite rapidly with phenyl isocyanate to form the corresponding urethan derivatives, but this reaction does not prove the presence of an isonitroso group in the original thio ether, for the isocyanate cannot differentiate with certainty between nitroso and isonitroso groups in compounds easily capable of tautomerization. A summary of the experimental details of this work is given in Table III. The mercaptide reaction, however, is not of general applicability; with some of the liquid, nitrogen tetroxide addition products, oxidative reactions occurred, resulting in formation of disulfides, as the main and sometimes the only product of reaction which could be identified.

Anhydrous, pure nitrogen tetroxide, distilled into cold ether solutions of trimethylethylene, in excess of equimolecular proportion, formed blue solutions from which bis-trimethylethylene nitrosate separated in varying yields. Typical results are given in Table I.

The maximum yield of bis-nitrosate (8.2%) appeared in experiment III, but under equally

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mixture. Wieland [*Ber.*, **54**, 1782 (1921)] stated that nitrogen tetroxide acts upon ether with formation of nitrous and nitric ethyl esters; accordingly, at least six reactants were present in Schmidt's experiments, which cannot be considered, therefore, as representing the addition of nitrogen tetroxide to trimethylethylene.

(4) Schmidt, *ibid.*, **35**, 2323 (1902).

(5) Klingstedt, *ibid.*, **58**, 2363 (1925).

(6) Demjanov, *Ann., Inst. Agronomique Mos.*, **4**, 155 (1899).

(7) T. Carlson, *Ber.*, **40**, 4191 (1907).

(8) Forster and Gelderen, *J. Chem. Soc.*, **99**, 239 (1911).

favorable conditions (II) the yield was 2% lower and only a negligible amount was formed in experiment I. No general relation can be discerned between the yield of bis-nitrosate and the experimental conditions. The yield of bis-nitrosate was invariably higher (35.2–39.2%) when petrol was used as diluent (experiments IV and V). Since the bis-nitrosate is difficultly soluble in petrol and only slightly more so in ether, the large variation between yields of bis-nitrosate formed in the two solvents cannot depend solely upon the slight difference between the solubility in the respective solvents. Without solvent, the amount of bis-nitrosate formed at −80° (experiment VII) was 5.8% lower than that produced at −7° (experiment VI) and 4.4% less than that formed slightly above room temperature in a gas phase reaction (experiment VIII). In these experiments, again, no direct relation appears between the yield of bis-nitrosate and the experimental conditions. Since in the absence of a diluent a variation of temperature of about 100° alters the yield of solid product by only 4.4%, the actual yield fluctuating between 43.2–47.6%, whereas the maximum yield produced in ether solution was only 8.2%, evidently, the effect of solvent upon the course of addition of nitrogen tetroxide to alkenes is far greater than that of the reaction temperature.

A comparison of the results obtained in petrol solution with those obtained without solvent, or in the gas phase, shows unmistakably that the degree of dissociation of the addendum has no material influence upon the extent of the bis-nitrosate formation. At −7°, without solvent, conditions under which the addendum consisted almost entirely of O_2N—ONO, 49% of the bis-nitrosate appeared, while in the gas phase, where the tetroxide was considerably more dissociated, almost the same percentage of the bis-nitrosate was formed; even at −80°, the proportion of bis-nitrosate differed but slightly. From these, and results with other ethylenic hydrocarbons, it is evident that the course of the addition depends only slightly upon the relative proportions in which the components of the addendum appear in the equilibrium, $2NO_2 \rightleftharpoons O_2N\text{—}ONO$; apparently, the dominant chemical factor is the relative polarity of the Δ-carbons of the alkene. In no experiment with trimethylethylene did we succeed in isolating a dinitro addition product, nor a corresponding dinitrite.

The green oils formed in petrol solution decomposed so easily that purification by fractionation was impossible, nor could the oily products obtained from the crude oils by benzoylation, or treatment with acetic anhydride and sulfuric acid, be identified. According to Schaarschmidt and Hofmeier,[9] the action of nitrogen tetroxide upon alkenes is more complex and the products less stable, the lower the reaction temperature. However, on adding the tetroxide to reaction mixtures cooled only to 0°, the yield of bis-nitrosate (39.2%) obtained approximated that found (35.2%) at −15°: the liquid products slowly decomposed, even at 0°, liberating a colorless gas and depositing a small amount of ammonium nitrate. Although decomposing slowly, the liquid product in one experiment was subjected to distillation at the pressure of a mercury pump and the volatile as well as the non-volatile oil treated with sodium thiophenylate in alcoholic solution, but organic sulfur derivatives suggestive of the constitution of the original, green addition product could not be isolated. Likewise, in the absence of diluent, other than excess trimethylethylene, green, unstable oils were formed which could not be identified: the oils deposited ammonium nitrate, at 0°, and decomposed with evolution of nitrous fumes when subjected to steam distillation. The green liquid distilled at the pressure of the mercury pump and at 30° to give a blue distillate and a non-volatile, yellow oil, neither of which could be identified directly, nor through the reaction products formed with sodium thiophenylate. We were, therefore, unable to determine whether these oils contained the blue product and the nitro-nitrite formed in the presence of ether.

The blue oil, formed by interaction of nitrogen tetroxide and trimethylethylene in ether solution, is a mixture and may be separated by distillation into an easily volatile, blue and a less volatile, greenish oil. A summary of a typical fractionation is given in Table II. Although the refractive index of the blue oil, purified by repeated fractionation, indicated that the material was nearly pure after one fractionation, yet the empirical constitution (approximate formula, $C_4H_6NO_2$) could not be established from the values obtained on analysis. Molecular weight determinations in freezing benzene gave the values 120 and 112, which indicate that the blue oil is monomeric

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[9] Schaarschmidt and Hofmeier, *Ber.*, **58**, 1047 (1925).

and of lower molecular weight than monomeric trimethylethylene nitrosate. The deep blue coloration is characteristic of monomeric nitroso derivatives, but, whereas the latter generally polymerize to crystalline solids, the purified, blue oils did not solidify at −80°. The catalyst and the experimental conditions were varied, but catalytic hydrogenation invariably stopped when relatively a small amount of hydrogen was absorbed and ammonia was the only reaction product identified; reduction with metals gave no better results. The blue oil is inert toward hot formic acid and 40% hydrobromic acid, did not react with phenyl isocyanate, nor with dimethylaniline. With phenylhydrazine and semicarbazide, oxidation occurred and the products could not be identified. Samples of blue oil separated from the reaction mixture by steam distillation had properties and gave results on analysis which compare favorably with those of preparations purified by low pressure distillation (Table II). In contrast, bis-trimethylethylene nitrosate is completely decomposed by steam distillation and under no conditions could it be depolymerized to a stable, blue oil. Attempts to convert the blue oil to a more stable product, by treatment with ozone, gave mixtures which could be separated only incompletely and could not be identified. Reduction of the blue oil with aqueous potassium hydrosulfide gave a complex mixture of products which could not be separated, nor could the nature of the main reaction product be established. The blue oil, isolated by methods which permit of semi-quantitative separation, constituted about 20–25% of the total reaction product.

By cooling the greenish-yellow oil, remaining as a residue after the liquid reaction product had been steam distilled, a crystalline, waxy solid (A), m. p. 60°, was obtained in low yield. The same material was subsequently isolated, in better yields, by cooling the greenish-yellow oil which was volatile with steam, or by diluting the original, liquid, reaction product with ether and cooling to −80°. The composition, $C_5H_{10}N_2O_4$, and the values (157 and 168) obtained in molecular weight determinations, together with the products, sodium nitrite and 3-nitro-2-methylbutanthiol-2-phenyl ether, quantitatively formed in the reaction with sodium thiophenylate, establish the structure of the waxy product as the nitrous ester of 3-nitro-2-methylbutanol-2. The quantitative details of the reactions which confirm the structure of the nitrous ester are given in Table III. Semi-quantitative isolation of the nitrous ester was not realized, but, based on the best separations, although steam distillation was employed entailing loss of about 15% of material, the minimum quantity produced in ether solution may be estimated as approximating 35% of the total reaction product.

The influence of a solvent upon the course of addition of hydrogen bromide to certain alkenes has long been known,[10] but in the above reaction the solvent exerts a decisive influence upon the chemical manner in which a reagent functions as an addendum. In petrol, or without solvent, the tetroxide functions with the component parts $—ONO_2 + NO$, yielding considerable amounts of the polymerized nitrosate; the oily by-products decomposed so easily that no pure compound could be isolated. On the other hand, the amount of bis-nitrosate formed in ether was relatively small, but the distillable oil contained up to 35% of the nitro-nitrite, formed by addition of the addendum components $—ONO + NO_2$ to the Δ-carbons.

Besides the blue oil and the nitrous ester, non-volatile, liquid products are formed constituting approximately 10% of the total reaction product. With sodium thiophenylate, no sulfur derivative indicative of the structure of the complex oil could be obtained. The molecular weight (208 and 307) of the non-volatile oil suggested that, in the presence of nitrogen tetroxide, trimethylethylene may have been polymerized to di- and triisoamylene and these acted upon by the tetroxide. Greenish-yellow oils were produced by the action of nitrogen tetroxide upon di- and triisoamylene, but, since no blue oils were formed, the products were not investigated. It is evident from the above results that the blue-green oil, formed by interaction of nitrogen tetroxide and trimethylethylene in ether, which Schmidt[2] believed to be the slightly impure monomeric nitrosate, is a complex product, from which as

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[10] The reversal of the mode of addition, observed in certain solvents [Ipatiev, *Jahresber.*, 738 (1903); 832 (1904); Michael and Zeidler, *Ann.*, **385**, 245 (1911); Sherrill, THIS JOURNAL, **56**, 926, 1645 (1934)], may be the effect of the solvent, or of peroxide influences [Kharasch, *ibid.*, **57**, 2463 (1935); **58**, 57 (1936); *J. Org. Chem.*, **1**, 393 (1936)], which may function by retarding the formation of the polymolecule normally leading to the maximal degradation of energy on decomposition, or, by accelerating the formation of the type of polymolecule leading to production of the isomeric derivative, normally always formed in subordinate quantity [Michael, *Ber.*, **39**, 2138–2163 (1906)].

TABLE II

	(A) 33 g. blue oil separated by low pressure distillation gave					
				Refractionation of (2) gave		
Fractions	(1)	(2)	(3)	(4)	(5)	(6)
G.	2.4	13.4	13.2 green residue	2.8	4.6	4.9 blue residue
B. p., °C.	>40	40–49		34–36	36–38	
Press., mm.	3	3		2	2	
$n^{9.5}\mathrm{D}$		1.4480				
$n^{20}\mathrm{D}$		1.4425		1.4410	1.4440	1.4450
d_{20}					1.0365	

Analysis of fraction (5): C, 49.01; H, 6.68; N, 14.63; mol. wt., 112.

yet only the isomeric, monomeric nitro-nitrite has been isolated in a perfectly pure condition.

Experimental

Nitrogen tetroxide was prepared by heating anhydrous lead nitrate, the evolved gas passed through a tube of phosphoric anhydride and condensed in a weighed ampoule.

Trimethylethylene was prepared by heating tertiary amyl alcohol with 10% hydrochloric acid, fractionating the distillate, removing the last traces of alcohol and water with sodium and refractionating.

Ether was dried with phosphoric anhydride and distilled. Petroleum ether (b. p. 20–40°) was washed, successively, with concentrated sulfuric and nitric acids, water, dried with phosphoric anhydride and distilled.

The reaction vessel, in all experiments excepting VII and VIII, consisted of a three-necked flask, provided with a stirrer, a calcium chloride tube and a tube suitably arranged so that connection could be made rapidly with the nitrogen tetroxide ampoule which, just previously, had been cooled to −30° and unsealed.

An all-glass arrangement of vertical, concentric tubes, shaped as nozzles,[11] was used in experiment VIII. The reaction chamber was 3 cm. long and 12 mm. in diameter and was sealed to 20 cm. of 10-mm. tubing, terminating in a 50-cc. bulb which, cooled to −30°, served as a condenser. By means of concentric nozzles suitably arranged, nitrogen tetroxide was diluted with dry nitrogen and entered the reaction chamber into which was simultaneously admitted a stream of nitrogen, previously passed through trimethylethylene contained in a Leyden flask cooled to 0°. Bis-trimethylethylene nitrosate collected in the vertical tube immediately below the reaction chamber and the green, oily product drained into the bulb condenser.

In experiment VII, nitrogen tetroxide was diluted with dry nitrogen, using the mixing apparatus described above, and then passed through an 8-mm. tube into the side neck of a two-necked flask, equipped with a stirrer and a calcium chloride tube.

With ether as solvent, the solid reaction product was filtered off, solvent removed at reduced pressure from the filtrate and the residual, blue oil steam-distilled, or distilled at the pressure of a mercury pump. With petroleum ether, the liquids were decanted from the bis-nitrosate, the solid triturated with ether, filtered off and the residual oil, recovered from the filtrate, combined with that decanted with the petrol solution. When no solvent was used the oily product was decanted, the solid washed with ether and the residual oil obtained from the filtrate combined with the decanted oil.

Separation of Liquid Products.—The liquids from two similar experiments were combined and the products separated by methods of which three typical examples are described. The low-pressure distillations were made in an all-glass apparatus, which was attached by a heavy rubber connector to a McLeod gage and a mercury vapor pump: distillation pressures were not recorded. A, B and C designate, respectively, the following compounds: the nitrous ester of 3-nitro-2-methylbutanol-2, 3-nitro-2-methylbutanthiol-2-phenyl ether and 3-nitro-2-methyl-2-phenylsulfone-butane.

Steam distillation of 55.6 g. of blue liquid gave (1) 25.8 g. of easily volatile, deep blue oil; (2) 13.9 g. of less volatile, greenish oil; and (3) 3.4 g. of residual oil. Distillate (1) was fractionated and gave 16.0 g. of deep blue distillate, b. p. 46–70° at 3 mm., leaving 6.8 g. of green, residual oil which, at −25°, deposited 1.5 g. of (A), m. p. 60°. *Anal.* Calcd. for $C_5H_{10}N_2O_4$: C, 37.05; H, 6.16; N, 17.3. Found: C, 37.23; H, 5.9; N, 16.6. The greenish oil (2) solidified at −25°, but only 3.2 g. of (A) could be isolated by filtration; the filtrate, diluted with ether and cooled to −80°, deposited 8 g. of crude (A), which was recrystallized from ether at −80° and gave 6 g. of pure product: mol. wt. calcd., 162. Found, in freezing benzene, (1) 157; (2) 168.

Low pressure distillation of 77 g. of blue oil yielded only 3.2 g. of blue distillate during three hours. The operation was discontinued, the residual, blue-green oil diluted with ether and cooled to −80° deposited 13.8 g. of (A). The oil (49.7 g.) from the filtrate was steam distilled and the oily distillate, cooled to −80°, gave 3 g. of (A). In another low pressure distillation, 71 g. of blue oil gave 24.0 g. of deep blue distillate, leaving 39.5 g. of greenish oily residue from which, after two recrystallizations at −80°, 6.7 g. of pure (A) was isolated. Three grams of (A) was added to a solution prepared from 0.8 g. of sodium, 20 cc. of methyl alcohol and 5 g. of thiophenol: the organic product (3.9 g.), insoluble in 10% alkali, distilled to give 3.2 g. of (B), b. p. 135° at 2 mm., which was treated with 3 g. of chromic anhydride in 10 cc. of glacial acetic acid and gave 3.1 g. of (C).

When steam distilled, the residual green oil (32.8 g.), from which the nitrous ester had been separated at −80°, gave (a) 20.8 g. of blue-green distillate and (b) 4.2 g. of viscous, yellow, residual oil. The blue-green oil (a) was fractionated: (1a) 3.3 g., of blue oil, b. p. 55–72° at 2 mm.; (2a) 16.2 g., nearly colorless oil, b. p. 80–100° (mostly at 87–100°) at 2 mm. Three grams of fraction (2a), treated with sodium thiophenylate as described above, gave, as the organic product, 3.7 g. of oil from which 3.5 g. of (B),

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(11) Horn, Polanyi and Style, *Trans. Faraday Soc.*, **30**, 190 (1934).

TABLE III

Expt.	Substance	G.	Reagent	G.	Solvent	Temp.	Time	Products	Yield		Properties, m. p., °C.
									Calcd.	Found	
I	(F)	3	C_6H_5SNa	2.4	CH_3OH	B. p.	10 min.	$NaNO_3$	1.58	1.5	
								(D)	3.8	3.3	90
II	(F)	2	C_6H_5SNa	1.6	CH_3OH	R. T.	8 days	$NaNO_3$	1.05	0.7	
								(D)	2.6	2.3	90
III	(F)	2	C_2H_5SN	1.1	C_2H_5OH	B. p.	10 min.	$NaNO_3$	1.05	1.0	
								(E)	1.99	2.0	60
IV	(F)	2	C_2H_5SNa	1.1	C_2H_5OH	R. T.	20 days	$NaNO_3$	1.05	1.0	
								(E)	1.99	1.5	59–60
V	(A)	2	C_6H_5SNa	1.6	CH_3OH	B. p.	15 min.	$NaNO_2$	0.85	0.8	
								(B)	2.78	3.0	
VI	(A)	2	C_6H_5SNa	1.6	CH_3OH	R. T.	6 days	$NaNO_2$	0.85	0.8	
								(B)	2.78	2.7	

NOTES ON TABLE III

D and E represent the phenyl and ethyl ethers, respectively, of 3-nitroso-2-methylbutanthiol-2; for reasons stated above, these compounds may have the isonitroso structure. F designates bis-trimethylethylene nitrosate, A, B and C the same compounds as before.

I. A suspension of (F) was heated with alcoholic sodium thiophenylate, most of the solvent removed and sodium nitrate filtered off. An ether solution of the filtrate was washed with water, dried and the solvent removed. The residual thio ether (D) melted at 90°. *Anal.* Calcd. for $C_{11}H_{15}NOS$: C, 63.16; H, 7.18; N, 6.7; S, 15.3; mol. wt. 209. Found: C, 63.25; H, 7.5; N, 7.15; S, (1) 15.9; (2) 15.4; mol. wt. (in freezing benzene), (1) 273, (2) 308. In ether solution, 1 g. of (D) and 0.6 g. of (D) (1 g.) and 0.6 g. of phenyl isocyanate gave 1.6 g. of addition compound, m. p. 113–114°. *Anal.* Calcd. for $C_{18}H_{20}N_2O_2S$: C, 65.85; H, 6.1; N, 8.54. Found: C, 65.87; H, 5.87; N, 9.1.

II. Products treated as above. *Anal.* Calcd. for $NaNO_3$: Na, 27.05. Found: Na, 26.9.

III. A suspension of (F) in a solution prepared from 0.3 g. of sodium, 25 cc. of alcohol and 0.8 g. of ethylmercaptan was heated, solvent distilled and sodium nitrate collected. *Anal.* Calcd. for $NaNO_3$: Na, 27.05. Found: Na, 27.3. The filtrate, in ether solution, was washed with water, dried and the solvent removed. The thio ether (E) was purified by sublimation at reduced pressure. *Anal.* Calcd. for $C_7H_{15}NOS$: S, 19.9; mol. wt., 161. Found: S, 20.3; mol. wt. (in freezing benzene), 231. In ether solution, 0.5 g. of (E) and 0.4 g. of phenyl isocyanate gave 0.8 g. of addition compound, m. p. 122°. *Anal.* Calcd. for $C_{14}H_{20}N_2O_2S$: N, 10.1; S, 11.43. Found: N, 10.12; S, 11.49.

IV. Bis-trimethylethylene nitrosate was suspended in a solution prepared from 0.3 g. of sodium, 25 cc. of alcohol and 1 g. of ethyl mercaptan. *Anal.* Calcd. for $NaNO_3$: Na, 27.05. Found: Na (1) 27.90; (2) 27.95. Solvent was removed from the filtrate, the residue, in ether solution, washed with water, dried and the solvent removed. The residual product (E) solidified completely.

V. A methyl alcohol solution of (A) and sodium thiophenylate was heated on the water-bath, most of the alcohol distilled and the sodium nitrite filtered off. *Anal.* Calcd. for $NaNO_2$; Na, 33.35. Found: Na, 33.23. Solvent was removed from the filtrate and the residual thio ether (B) distilled at 1 mm. with the bath temperature at 170°.

VI. Sodium nitrite (0.5 g.) was filtered off: the alcoholic filtrate, after concentration, yielded 0.3 g. of sodium nitrite. Both portions were analyzed. *Anal.* Calcd. for $NaNO_2$: Na, 33.35. Found: Na (1) 33.3; (2) 33.25. The liquid thio ether (B), treated with 2.7 g. of 30% hydrogen peroxide in acetic acid, was recovered unchanged; oxidized with 2.7 g. of chromic anhydride in 10 cc. of hot acetic acid, gave the sulfone (C) (2.3 g.), m. p. 102–103°. *Anal.* Calcd. for $C_{11}H_{15}NO_4S$: C, 51.4; H, 5.84. Found: C, 51.25; H, 5.84.

b. p. 132° at 2 mm., was obtained, oxidation of (B) with chromic anhydride, after two treatments, yielding 1.9 g. of (C).

The oil, non-volatile with steam, gave the value 307 in a molecular weight determination in freezing benzene. Incomplete separation may account for the lower value (208), found for the residual oil remaining after the liquid product had been distilled at low pressure.

The easily volatile, deep blue oil, isolated by steam or low pressure distillation, was fractionally distilled, using a jacketed column of beads. A typical fractionation is give in Table II.

(B) Properties of Blue Oil Separated by Steam Distillation.—B. p. 43–47° at 2 mm.; $n^{9.5}_D$ 1.4512; d_{20} 1.044; mol. wt., 120. Analysis of three preparations gave the average results: C, 48.72; H, 7.25; N (one determination), 12.58.

Table III is a summary of the data obtained in the study of the action of sodium mercaptides upon bis-trimethylethylene nitrosate and the nitrous ester of 3-nitro-2-methylbutanol-2.

Summary

1. The action of nitrogen tetroxide upon trimethylethylene has been re-investigated. The course of the reaction varies slightly with the temperature but greatly with the solvent. In ether, comparatively little bis-trimethylethylene nitrosate is formed; the yield of the latter varied from 28–39% in petrol and without solvent from 42–49%, although the temperature varied from −80 to 30°. Since the proportion of NO_2 to O_2NONO in the system $2NO_2 \rightleftarrows O_2NONO$ increased considerably, the course of formation of bis-nitrosate is relatively independent of the degree of dissociation of the addendum.

2. The liquid reaction product formed in petrol solution, or without solvent, is unstable and decomposed on vacuum distillation. The chemical nature of the oil could not be established.

3. The blue-green liquid formed in ether solution, contrary to the conclusion of Schmidt, is

not, or to any appreciable extent, the monomeric trimethylethylene nitrosate. The blue coloration is caused by a distillable, blue liquid, constituting only 20–25% of the total reaction product, which could not be polymerized, nor solidified at −80°. Oxidation as well as addition apparently enters into its formation. The remainder of the liquid reaction product is composed of the nitrous ester of 3-nitro-2-methylbutanol-2, constituting at least 35% of the total reaction product, and high boiling, complex oils, representing 10% of the total product, which could not be characterized.

CAMBRIDGE, MASS. RECEIVED JANUARY 26, 1937

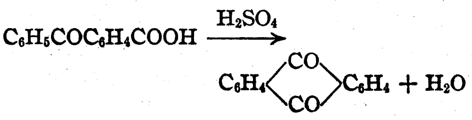
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

A Kinetic Study of the Sulfuric Acid Condensation of *o*-Benzoylbenzoic Acid[1]

BY CHARLES W. DEANE

Both for considerations of kinetic theory and for its practical interest as the principal step in the industrial synthesis of the dye intermediate, anthraquinone, an extension of the velocity measurements on the decomposition of *o*-benzoylbenzoic acid, particularly in fuming sulfuric acid concentrations, appears especially valuable.

The major historical points appeared in an earlier report[2] on this reaction



$$C_6H_5COC_6H_4COOH \xrightarrow{H_2SO_4} C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}C_6H_4 + H_2O$$

Since 1929 Wiig,[3] also Hammett and his co-workers,[4,5] have used the data upon *o*-benzoylbenzoic acid in dealing, respectively, with Taylor's theory of negative catalysis and with correlations of the kinetics to the acidity function, H_0.

With reference to Fig. 1, a graphical analysis using the data of Gleason and Dougherty shows that rather than as reported to the contrary,[2] *o*-benzoylbenzoic acid is not exceptional, but is like oxalic acid in having the velocity constant k, as a logarithmic or exponential function of the water present. The extra dotted line shows the result of using Gleason and Dougherty's kinetic value obtained at a decomposition of but 4% which resulted from employing an inflexible four-hour period to measure the reaction rate.

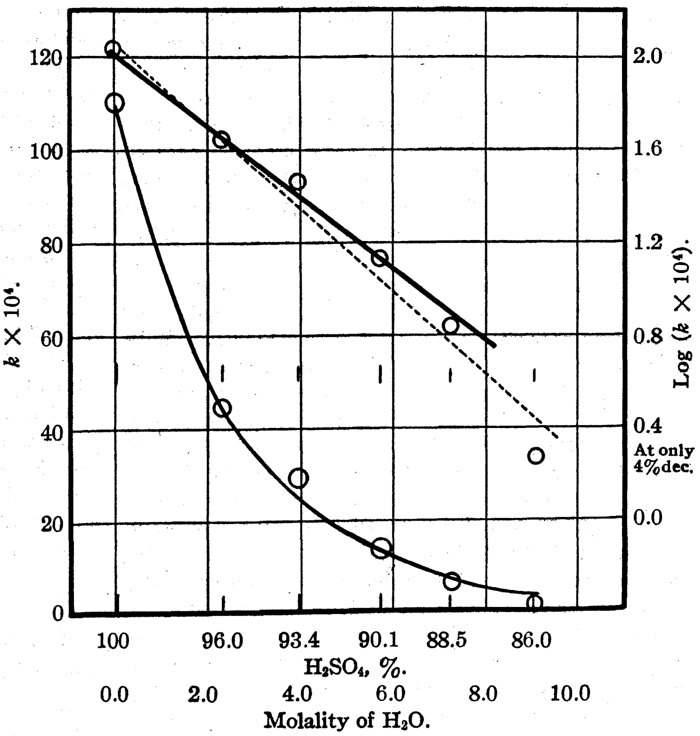


Fig. 1.—The velocity constant k for the condensation of *o*-benzoylbenzoic acid by sulfuric acid at 75°. Analysis of data obtained by Gleason and Dougherty.[2]

The main objectives in the present work have been to extend the data by certain basic improvements in the general method of Gleason and Dougherty,[2] and to obtain precise results at the far higher reaction speeds due to fuming sulfuric acid. This extension of data was undertaken to check general theoretical predictions of the kinetic effects[3] in the unexplored regions of fuming sulfuric acid.

Among the exceptional features and advantages afforded by this reaction for kinetic studies

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[1] The summary of a thesis presented to the Graduate School of The University of Rochester in partial fulfilment of the requirements for the degree of Master of Science.

[2] Gleason and Dougherty, THIS JOURNAL, **51**, 310 (1929).

[3] Wiig, *ibid.*, **52**, 4742 (1930).

[4] Hammett, *Chem. Rev.*, **16**, 67 (1935).

[5] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

are: a single reaction product, besides the equivalent of water, results; this is obtained instantaneously by a dilution of the reaction mixture, and accurate gravimetric measurements are possible; the reactants and products remain in the liquid phase; the substrate concentrations employed can be relatively very high; any slight side products of the reaction play in it a very negligible part.

Experimental Part

Preparation and Purification of Materials.—The following method of purifying *o*-benzoylbenzoic acid, similar to that used in the Eastman Synthetic Laboratories, is based on 500 g. of the original material. In a 1-liter wide-mouthed flask heat over a free flame to about 80° with mechanical stirring, 335 g. (5.55 moles) of glacial acetic acid (99.9%, m. p. 16.6°, sp. gr. 1.05). A current of air properly blown around the neck of the flask prevents any acetic acid vapors from flowing down around the flask to the heat source and igniting. With the temperature of the acetic acid at 80–85°, slowly add 500 g. (2.38 moles) of *o*-benzoylbenzoic acid, m. p. 127°. After continued stirring until this acid is dissolved, filter the mixture through flannel. While the filtrate is still hot pour it into a 2-liter flask and add cold water until the solution commences to become cloudy. Now add no more water until crystals of *o*-benzoylbenzoic acid begin to appear, which with mechanical stirring occurs within five minutes. At this point add slowly more cold water (if water is added too rapidly, undesirable large lumps of an *o*-benzoylbenzoic acid aggregate form) until the 2-liter flask is filled. With external cooling by a water jet, continue mechanical stirring until the mixture is cold. Filter the crystals by suction, and wash well to remove any remaining acetic acid. Accomplish the removal of the last water in a hot cabinet, drying the material at 105–110° on glass or porcelain.

The purified *o*-benzoylbenzoic acid when dry melted at 127.2–128.5° (corr.). Both Richter's "Lexikon" and the "International Critical Tables" give a m. p. of 127° for water-free material. Tests on the above purified material by twelve hours of drying at 110–115° showed a loss of weight of less than 0.2%. The water-absorbing power of this material on exposure to ordinary laboratory conditions of humidity was negligible (0.002%). Before purification, this material, upon heating for four hours in an oven at 110–115°, proved to be 3 to 5% volatile. Because the *o*-benzoylbenzoic acid furnished (Eastman product) became a deep brown on solution in sulfuric acid it was conjectured that, despite a sharp melting point, small aggregates of foreign materials might be causing coloration, or that possibly a breakdown and carbonization was occurring. Tests on the carefully purified materials, however, resulted in colored solutions both for anthraquinone and for *o*-benzoylbenzoic acid. This is in line with the basis of recent colorimetric determinations of acidity in the highly concentrated acids[4,5] in which slight concentrations of anthraquinone are used as indicators.

Three lots of sulfuric acid corresponding to 94.86, 100.42 (1.8% fuming), and 105.92% (26.2% fuming) were employed. Except for the first, these were prepared by mixing c. p. 95% sulfuric acid with Baker and Adamson reagent quality fuming sulfuric acid, 30%, in the calculated proportions for approximating the desired strengths. By precipitation as barium sulfate four samples of each were analyzed, due precautions being taken in weighing and manipulation to prevent either sulfur trioxide loss or moisture absorption. An independent and fuller check, as it included the calculating and mixing procedure universally employed in the experiments to obtain the sulfuric acid strengths used, was obtained by mixing in the calculated proportions 94.86 and 100.42% sulfuric acid for a 100% acid, and taking its melting point. By a triple determination this was 10.38°, or the acid thus proved to be within 0.1% of 100% by comparison with a plot of the data of Hantzsch[6] in which per cent. water concentration in the sulfuric acid was plotted against the melting point.

Apparatus and Procedure.—Solutions of *o*-benzoylbenzoic acid in sulfuric acid of the desired strength were prepared in 200-cc. round-bottomed flasks provided with propeller stirrers and adequately protected against the access of moisture from the air. In general 8.1021 g. of the ortho acid was added to 35 cc. of sulfuric acid solution at the reaction temperature and the stirring started. Independent tests showed that within six to nine minutes thereafter the temperature of the solutions came within one-tenth of a degree of that prevailing in the surrounding thermostat (constant within 0.1°), whereupon an initial sample was removed. Subsequent samples were removed by means of a 5-cc. pipet at 0.25, 0.40, 0.60, and 0.75 of the life period of the reaction, delivered into 100 cc. of water and analyzed according to the procedure of Gleason and Dougherty,[2] except that an asbestos mat in a Gooch crucible was employed for filtration.

The initial concentration, *a*, was ascertained in two ways; either by analysis after allowing the reaction to go to completion in triplicate samples, or by calculation from the original amounts of ortho acid added, correcting in each case for the expansions due to the temperature change and to the addition of the ortho acid. These corrections were at 75° 19.6 and 20.0%, and at 85° 20.1 and 20.4%, for 98.0 and 105.9% sulfuric acid, respectively.

Results

Completeness and Order of the Reaction.—Quantitative yields of anthraquinone from *o*-benzoylbenzoic acid have been reported.[2] In 8% fuming sulfuric acid, the author found the yields above 99%; however, at concentrations above 20% fuming acid, yields fell to 97–98%.

A set of typical kinetic measurements and the computed velocity constants, assuming a unimolecular reaction, appear in Table I.

As can be seen from the last column, the value of the constant decreases slightly as the reaction progresses, doubtless due to the water formed during the reaction. Further proof that the reaction is indeed unimolecular was obtained

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(6) Hantzsch, *Ber.*, **55**, 953 (1922); **63**, 1782 (1930).

TABLE I

A TYPICAL EXPERIMENT AT 75°

Sulfuric Acid = 100.4% (SO_3 = 1.8%)

Equiv. wt. anthraquinone at "zero" time in 5 cc. of solution = 0.7599 g. = a

t, min.	*a* − *x*	$k \times 10^4$, min.$^{-1}$
20.0	0.5894	127.0
40.2	.4572	126.4
50.0	.4081	124.4
65.0	.3541	121.8
		Average, 124.9 or 125

by similar experiments at half the ortho acid concentration above, when values resulted whose average was 125.1.

The Effects of Water and of Sulfur Trioxide on the Reaction Rate.—Based on previous findings of sulfur trioxide and of water as negative inhibitors upon the oxalic, malic and the citric acid decompositions,[7–9] a maximum rate of decomposition would be expected with *o*-benzoylbenzoic acid. Tables II and III summarize the average velocity constants for each set of experiments at 75 and 85°. The mean deviation of the half-life average *k*'s is less than 0.4%, and at comparable points, the data agree well with the values of Gleason and Dougherty.[2] These determinations indicate that the ortho acid is really an exceptional case to the predicted maximum[3] based on Taylor's theory of negative catalysis.[10]

TABLE II

THE EFFECTS OF WATER AND OF SULFUR TRIOXIDE AT 75°

Molality of *o*-benzoylbenzoic acid = 0.55

% H_2SO_4	Molality H_2O	Molality SO_3	Average values of $k \times 10^4$ for each experiment		Final av. $k \times 10^4$
96.0	2.314		48.1		48.1
98.0	1.134		77.3	77.7	77.5
100.0	0.000	0.000	118.7	117.6	118
100.4		.233	124.9	124.9	125
101.8		1.086	128.3–129.0	129.1	129
103.16		2.033	135.8	136.3	136
104.5		3.122	145.5	144.7	145
105.9		4.434	170.4	171.0	171

TABLE III

THE EFFECTS OF WATER AND OF SULFUR TRIOXIDE AT 85°

Molality of *o*-benzoylbenzoic acid = 0.55

% H_2SO_4	Molality H_2O	Molality SO_3	Average values of $k \times 10^4$ for each experiment		Final av. $k \times 10^4$
98.0	1.134		227.1	229.3	228
100.0	0.000	0.000	344.1	342.8	343
100.4		.233	373.3	375.1	374
101.8		1.086	380.6 380.8	383.1	381
103.2		2.033	384.1 386.8	385.0 381.8	384
104.5		3.122	416.7	419.1	418
105.4		3.944	441.2	436.8	439
105.9		4.434	458.1	456.4	457
106.5		5.055	477.8	486.2	481

Figure 2 shows the relative effects of water and of sulfur trioxide upon the logarithm of the velocity constant, *k*. Up to the 100% point, the molality (moles per 1000 g. of solvent) of the inhibitor, water, plotted against the logarithm of *k* gives a straight line. Beyond the 100% point, the slope of the line lessens considerably, being nearly horizontal from 2% fuming acid to approximately the 14% point. Despite special experimental care, no peak was found at 14% sulfur trioxide, which point may possibly be the maximum for oxalic acid.[7] At 14% fuming acid and higher, the decomposition curve for *o*-benzoylbenzoic acid rises to assume a slope approximately one-fifth of the slope caused by a corresponding decrement in the molality of water below the 100% sulfuric acid point.

The Effect of Temperature on the Reaction Rate.—The development of a correlation of kinetic data with various postulated factors and mechanisms may be aided considerably by data on the temperature coefficient, and by a tabulation of *E*, the energy of activation. These values are given in Table IV for which the data of Tables II and III have been used to derive the values presented. The values of *E* were calculated from the following integrated form of the Arrhenius equation

$$E = \frac{1.98 \times T_2 \times T_1 \times \log k_2/k_1 \times 2.303}{T_2 - T_1}$$

The ratio of k_2/k_1 was evaluated by a large scale

TABLE IV

ENERGIES OF ACTIVATION AND TEMPERATURE COEFFICIENTS (FOR 75 TO 85°)

% H_2SO_4	Molality H_2O	Molality SO_3	k_2/k_1	*E*, cal.
98.0	1.134		2.94	26,700
100.0	0.000	0.000	2.92	26,400
100.4		.233	2.97	26,900
101.8		1.086	2.96	26,800
103.2		2.033	2.98	26,900
104.5		3.122	2.84	25,800
105.4		3.244	2.74	24,900
105.9		4.434	2.70	24,500
			Av. *E* =	26,100

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(7) Wiig, THIS JOURNAL, **52**, 4737 (1930).

(8) DeRight, *ibid.*, **56**, 618 (1934).

(9) Wiig, *ibid.*, **52**, 4729 (1930).

(10) Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

plot of Fig. 2 on cross section paper. A computation of the data of Gleason and Dougherty yields temperature coefficients of 3.2 and 3.4, respectively, for the intervals 85–75° and 75–65° at 96% sulfuric acid. The results presented here indicate a temperature coefficient somewhat below three, as shown in Table IV, but the agreement is reasonably satisfactory. It is to be noted that the sulfur trioxide, *acting as a positive catalyst*, diminishes the temperature coefficient.

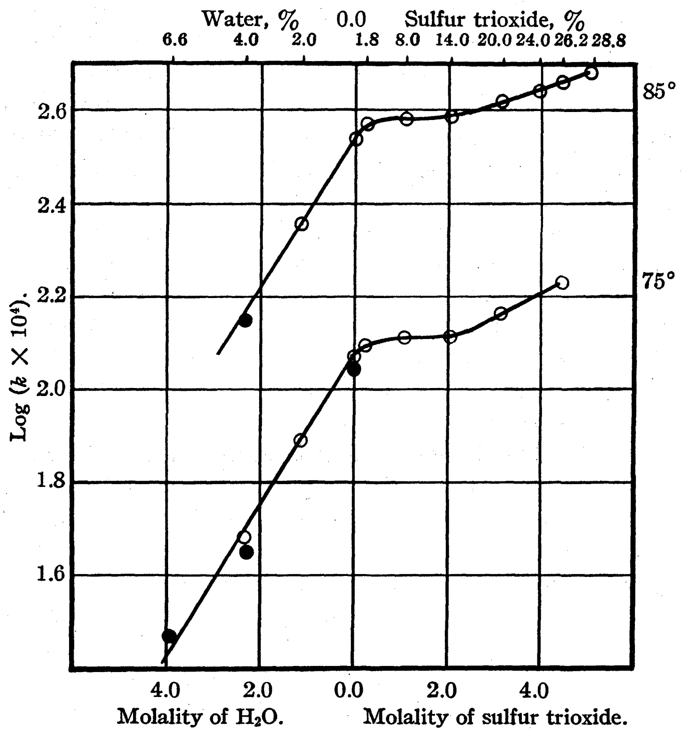

Fig. 2.—The velocity constant k for the condensation of *o*-benzoylbenzoic acid by sulfuric acid at 75 and 85°: ●, Gleason and Dougherty, ○, Deane.

Discussion

Figure 3 compares the effects of corresponding molalities of water and of sulfur trioxide upon the rates of decomposition of three organic acids with sulfuric acid. Table V lists these acids and states the widely variant effects of the catalysts upon the decomposition velocities. The unusual feature for *o*-benzoylbenzoic acid is the behavior of sulfur trioxide, particularly in fuming acid concentrations above 14%, as a positive catalyst.

TABLE V

COMPARISON OF THE INHIBITING POWER OF WATER AND OF SULFUR TRIOXIDE UPON THE DECOMPOSITION OF ORGANIC ACIDS

Organic acid	Relative inhibiting power For water	For sulfur trioxide
Oxalic	++, very strong	o, weak, if at all
Malic	++, very strong	++, very strong
o-Benzoylbenzoic	o, +, quite weak	o, − not inhibition, but acceleration

Possible correlations on the basis of effective ionic and molecular concentrations to explain the sulfuric acid decompositions of the organic acids are now considered. Because organic oxygen compounds are highly ionized basically in strong sulfuric acid, it is possible that factors of acid–base catalysis are effective. Assuming that the hydrogen ion concentration is related to reaction velocity, then the kinetic data on *o*-benzoylbenzoic acid indicate an increasing acidity in fuming sulfuric acid. An interesting question is the validity of this correlation above 100% sulfuric acid. Thus, to test whether the hydrogen ion concentration in terms of the acidity function H_0,[5] is a prime variable, its measurement in fuming sulfuric acid is in order. Because of the variant kinetic features exhibited by the oxalic and malic acid decompositions (Fig. 3 and Table V) it definitely appears that other phenomena predominate, and that these reactions are *not* governed by simple ionic factors.

To consider the kinetics of *o*-benzoylbenzoic acid from the molecular standpoint up to 28.8% fuming sulfuric acid, also, the extent of the determinations is limited. Of the five organic acids[1,7,9,11,12] only the oxalic acid study[7] presents data over a sufficient range to permit general comparisons with the kinetics of the *o*-benzoylbenzoic acid.[13] In Fig. 3 it will be noted that the ortho acid rate remains nearly horizontal from approximately 2 to 14% fuming acid. This 14% point also appears the point of maximum decomposition velocity for oxalic acid. Above 14% sulfur trioxide, however, a marked difference is to be noted: the oxalic acid decomposition is probably very slightly inhibited, while that of *o*-benzoylbenzoic acid is definitely accelerated by additional sulfur trioxide.

To explain these phenomena molecularly, the oxalic acid behavior up to the 14% point is due

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[11] (Formic), DeRight, THIS JOURNAL, **55**, 4761 (1933).

[12] (Triphenylacetic), Dittmar, *J. Phys. Chem.*, **33**, 533 (1929).

[13] However, it may be noted that in the cases for citric and malic acids, the reaction in fuming sulfuric acid at 14% sulfur trioxide approaches zero rate at room temperatures.

to the decreased water (a very strong inhibitor here) in the fuming sulfuric acid by the increase of sulfur trioxide. Above 14% sulfur trioxide the reaction is that of oxalic acid with sulfuric acid, slightly inhibited by the sulfur trioxide. This is in accord with Taylor's theory of negative catalysis.[10]

To rationalize the exceptional *o*-benzoylbenzoic acid, a new case may be postulated in that the predominant reaction above the 14% point is the decomposition caused by sulfur trioxide itself, or by pyrosulfuric acid. No inhibiting complex with sulfur trioxide is effective, so that Taylor's theory of negative catalysis does not here apply in fuming sulfuric acid above 14% sulfur trioxide.

Below 14% sulfur trioxide the same mechanism may apply for *o*-benzoylbenzoic acid as for oxalic acid. By Fig. 3 and Table V water is shown a relatively weak inhibitor for *o*-benzoylbenzoic acid. An explanation, then, as to why its curve (Fig. 3) remains flat to about 14% sulfur trioxide follows: the inhibiting water is furnished by the equilibrium $H_2SO_4 \rightleftarrows SO_3 + H_2O$. Owing to a displacement of this to the right by temperatures of 75 and 85°, the experiments for *o*-benzoylbenzoic acid require a strength of about 14% sulfur trioxide to overcome the water resulting from the dissociation at these higher temperatures.

A mechanism for the decomposition of *o*-benzoylbenzoic acid by sulfuric acid has been proposed by Gleason and Dougherty.[2] Their velocity measurements upon which this was partly based, however, were not such as would disclose the slowing down of the reaction during its course because the reaction speed is relatively quite insensitive to the slight amount of water formed. Inasmuch as the decrease of *k* as shown in Table I consistently occurred in all these experiments, the fast reaction they postulated because of no falling off of the rate receives no support here. The proposed intermediate reaction may take place but probably is not instantaneous.

From the industrial angle, the kinetic data above reported deal directly with a principal step in the production of anthraquinone. By the data presented, comparisons can be made of the relative condensing powers of concentrated and fuming sulfuric acids.

The author wishes to express his heartfelt appreciation to Dr. Edwin O. Wiig for his helpful suggestions and sincere interest in the progress of this work.

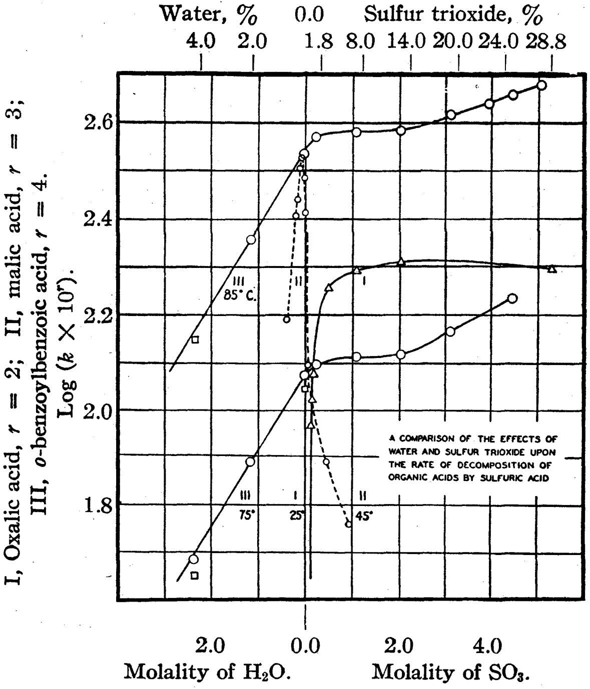

Fig. 3.—A comparison of the effects of water and of sulfur trioxide upon the rate of decomposition of organic acids by sulfuric acid.

Summary

This investigation of the decomposition velocity of *o*-benzoylbenzoic acid in concentrated and fuming sulfuric acid presents (1) an adequate method of determining the reaction rates in fuming sulfuric acid; (2) a suitable means of purifying *o*-benzoylbenzoic acid; (3) experimental evidence that the reaction follows the unimolecular law, and that yields are quantitative; (4) a check of earlier determined reaction rates and new reaction rate data, with energies of activation, for the decomposition of *o*-benzoylbenzoic acid in 98 to 106.5% sulfuric acid at 75° and 85°; (5) the discovery that, unlike other organic acids studied to date, *o*-benzoylbenzoic acid has no maximum decomposition velocity for a definite water or sulfuric trioxide concentration; and that sulfur trioxide at concentrations above 14% acts as a positive catalyst; (6) theories for the reaction mechanism briefly discussed and an explanation of the observed kinetics.

NEW YORK, N. Y. RECEIVED JANUARY 30, 1937

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Condensations of Aromatic Amines with Formaldehyde in Media Containing Acid. VII. The Polymeric States and Structures of Some Anhydro-*p*-(alkylamino)-benzyl Alcohols

BY W. S. YOUNG AND E. C. WAGNER

Anhydro-*p*-alkylaminobenzyl alcohols of the type $\left[{}^{\text{R}}{>}\text{NC}_6\text{H}_4\text{CH}_2\text{—}\right]_n$, or their salts, have been reported from six alkylarylamines, *viz.*, methyl-, ethyl-, *n*-propyl-, *n*-butyl-, isoamyl- and benzyl anilines.[1-4] Only the methyl, ethyl and benzyl compounds have hitherto been isolated as bases,[2,4] and of these only the first has been well characterized. Friedländer[4] found for the methyl compound a molecular weight of 224, and reported it to be dimeric. He established its essential structure by reduction to methyl-*p*-toluidine. In like manner the salts of other bases of this type were shown[3] to have the same structure.

Knowledge of the anhydro-*p*-alkylaminobenzyl alcohols is so meager that a more careful characterization of the compounds mentioned was undertaken. The six bases were isolated in a state of purity from the purified hydrochlorides. Their essential structural identity was shown by reduction to the corresponding alkyl-*p*-toluidines. Molecular weight determinations in benzene, with precautions to minimize error due to moisture absorbed from the atmosphere, failed to confirm Friedländer's value for anhydro-*p*-methylaminobenzyl alcohol. This base, and all the others, were found to be trimeric, *viz.*, $\left[{}^{\text{R}}{>}\text{NC}_6\text{H}_4\text{CH}_2\text{—}\right]_3$. A cyclic structure is probable and would be strain-free.[5] Molecular weights determined in molten camphor were much higher, indicating further polymerization by heat. The bases, and to a less degree the hydrochlorides, are not very stable and on keeping acquire a yellow to orange color. Table I presents molecular weights, melting points and analytical values for the six bases. Results of the reduction experiments are mentioned in the experimental part.

The six bases were made also by the use of methylal instead of formaldehyde. A temperature of about 50° was necessary to disengage formaldehyde in the reaction mixtures, and as this temperature was favorable also to the formation of diphenylmethane bases[6] the method appeared to be without advantage.

Experimental

General.—The alkylanilines used were redistilled Eastman Kodak Company products; benzylaniline was a Kahlbaum specimen.

Boiling points of alkyl-*p*-toluidines obtained in the reduction experiments were determined by Siwoloboff's method.

Molecular weights in benzene were determined with a P. T. R. Beckmann thermometer in the presence of anhydrous barium perchlorate, as recommended by Rall and Smith,[7] and with an air-sealed mechanical stirrer to minimize interference by atmospheric moisture. The cryoscopic constant of the benzene was determined using pure naphthalene. Molecular weights in camphor were determined by the procedure of Rast, using a turpentine thermometer.

Preparation of Hydrochlorides of Anhydro-*p*-alkylaminobenzyl Alcohols.—The method described previously[3] was employed with slight changes as required in individual cases. Salts of the methyl-, ethyl-, *n*-propyl- and *n*-butyl compounds were made in water solution. To obtain the hydrochlorides of the isoamyl and benzyl bases it was found better to dissolve the alkylaniline in several parts of U. S. P. alcohol, add a slight excess of concd. hydrochloric acid, dilute with water and then add to the chilled mixture the required formalin. Benzylaniline separated at first as its hydrochloride, which dissolved progressively as the anhydro-*p*-benzylaminobenzyl alcohol hydrochloride formed and crystallized out.

The filtered anhydro-*p*-alkylaminobenzyl alcohol hydrochlorides were washed thoroughly with alcohol and then ether. This operation was found to be important, especially with the *n*-butyl and isoamyl compounds, whose salts were slimy as first obtained. The alcohol and ether removed resinous or oily impurities which otherwise later contaminated the isolated bases and impeded their crystallization. The salts so obtained were pure white, and unlike specimens prepared without effective washing,[3] approached analytical purity.

Preparation of the Anhydro-*p*-alkylaminobenzyl Alcohol Bases.—The washed and dried salt was suspended in about five parts of alcohol chilled in ice. The mixture was stirred mechanically and 20% aqueous sodium hydroxide solution was added slowly to alkalinity. Stirring and chilling were

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(1) Goldschmidt, *Chem.-Ztg.*, **24**, 284 (1900); **26**, 606, 967 (1902).

(2) German Patent 97,710, *Friedl.*, **5**, 94 (1901).

(3) Wagner, THIS JOURNAL, **55**, 724 (1933).

(4) Friedländer, *Monatsh.*, **23**, 973 (1902).

(5) Private communication from Dr. E. H. Cox, of Swarthmore College. Construction of the cyclic trimer, using precision atomic models, showed the molecule to be entirely strain-free.

(6) Von Braun, *Ber.*, **41**, 2145 (1908); Rivier and Farine, *Helv. Chim. Acta*, **12**, 865 (1929); Wagner, THIS JOURNAL, **56**, 1944 (1934).

(7) Rall and Smith, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 324 (1936).

TABLE I

SOME ANHYDRO-*p*-ALKYLAMINOBENZYL ALCOHOLS

Compound $R\rangle NC_6H_4CH_2—$ R	M. p. (corr.) °C.	Molecular weights In benzene found[a]	Calcd. trimer	In camphor	Analyses Carbon,[f] % Calcd.	Found	Hydrogen,[f] % Calcd.	Found	Nitrogen, % Calcd.	Found
Methyl	209–12[b]	351[c]	357	2070					11.8	11.4[g]
Ethyl	84–6[d]	396	399	1500					10.5	10.4[g]
n-Propyl	106–8	447	441	1350	81.6	81.6	8.84	8.83	9.5	9.35[g]
n-Butyl	52–3	484	483	1670	82.0	81.8	9.32	9.25	8.7	8.7[h]
i-Amyl	46–8	508	525	1470	82.3	82.2	9.71	9.73	8.0	8.3[h]
Benzyl	162–3[e]	579	585	1570	86.2	86.1	6.67	6.56	7.2	7.1[g]

[a] Averages of from two to five values. [b] Previously reported[2,3]: 210°, 205–210°. [c] Friedländer[4] found 224. [d] Previously reported[2,4]: 86°, 79–80°. [e] Previously reported[2]: 161°. [f] Semi-micro method. Analyses by Wm. McClellan. [g] Semi-micro Kjeldahl method. Analyses by F. W. Landau. [h] Micro Dumas method. Analyses by Edw. D'Ouville.

continued some minutes longer, and any lumps of base were broken up. The mixture was treated with several volumes of ice water, and the precipitated base was filtered off and washed with cold 50% alcohol. It was dried in a vacuum desiccator and then crystallized. The methyl compound was satisfactorily crystallizable from benzene, and the other compounds from ligroin (70–90°). The *n*-butyl and isoamyl compounds were very soluble in ligroin, and their recovery necessitated evaporation of part of the solvent; the isoamyl compound required considerable manipulation to induce crystallization.

The bases were crystalline and white, but became discolored on standing. Melting points were not in all cases sharp; it is possible that melting was accompanied by incipient decomposition or by change in polymeric state. The melting points of homologous bases showed "alternation."

Reduction of Anhydro-*p*-alkylaminobenzyl Alcohols to Alkyl-*p*-toluidines.—Reduction was effected using zinc dust and hot dilute sulfuric acid as previously described.[3] The alkyl-*p*-toluidines from new bases were identified by their boiling points and by melting points of their hydrochlorides. The values obtained were as follows: (1) *n*-propyl-*p*-toluidine, b. p. 237–240°; hydrochloride, m. p. 154–155°, (2) *n*-butyl-*p*-toluidine, b. p. 251–252°; hydrochloride, m. p. 148–149°, (3) isoamyl-*p*-toluidine, b. p. 266–267°; hydrochloride, m. p. 139–142°, (4) benzyl-*p*-toluidine, b. p. 318–320°; hydrochloride, m. p. 180–181°. The hydrochlorides of *n*-butyl- and isoamyl-*p*-toluidines were identified also by mixed melting point tests.

Summary

1. Three new bases of the anhydro-*p*-alkylaminobenzyl alcohol series have been prepared, and together with three bases previously known, have been characterized with respect to polymeric state and structure.

2. The six bases were found to be trimeric in benzene solution, a finding at variance with Friedländer's conclusion that anhydro-*p*-methylaminobenzyl alcohol is dimeric. In molten camphor polymerization was found to be extensive. Strong reduction split the bases into the corresponding alkyl-*p*-toluidines, showing them to have the structure $\left[{}^{R}\!\rangle NC_6H_4CH_2—\right]_3$.

PHILADELPHIA, PENNA. RECEIVED FEBRUARY 16, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Alkenyl Esters Derived from Alkylacetylenes[1]

BY STEFAN J. SLANINA AND G. F. HENNION

Introduction

It was reported in a previous paper[2] that addition of bromine to the 2-acyloxy-1-alkenes derived from alkylacetylenes was followed by spontaneous cleavage yielding an acyl bromide and a monobromomethyl alkyl ketone. Further study has revealed that a number of other agents effect similar cleavage.

As in the case of bromination these esters react readily with hydrogen bromide and chloride. The addition compounds are unstable and cleave to yield the acyl halide and corresponding methyl alkyl ketone. The reactions may be represented as

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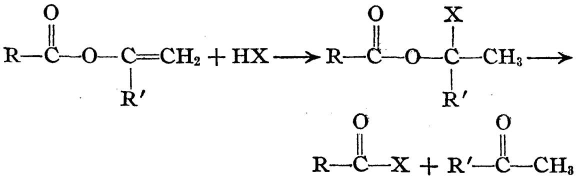
(1) Paper XX on the chemistry of the alkylacetylenes and their addition compounds; previous paper, *J. Org. Chem.*, **1**, in press (1937).

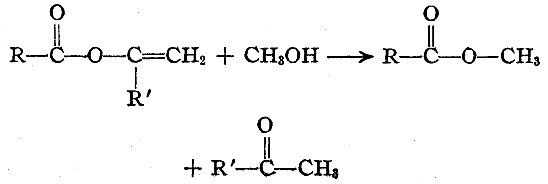
(2) Slanina, Hennion and Nieuwland, THIS JOURNAL, **58**, 891 (1936).



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{R'}{\underset{|}{C}}{=}CH_2 + HX \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{R'}{\underset{|}{\overset{X}{\overset{|}{C}}}}{-}CH_3 \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}X + R'{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

The intermediate halogen esters were not isolated. When hydrogen bromide was used, however, there was obtained, in addition to the two products indicated in the above equation, a small quantity of unidentified high-boiling material. Tests for bromine were negative. A corresponding substance was not obtained when 2-(chloroacetoxy)-1-hexene was treated with hydrogen chloride.

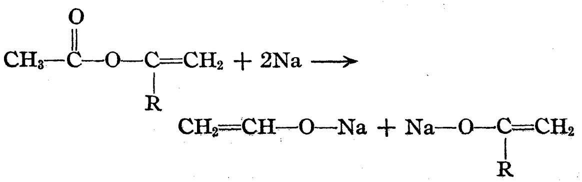
The alkenyl esters alcoholize readily when either *p*-toluene sulfonic acid or sodium methylate are employed as catalysts.



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{R'}{\underset{|}{C}}{=}CH_2 + CH_3OH \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_3 + R'{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

When such an ester and sodium methylate were mixed in molar proportions the reaction was extremely violent and apparently yielded the sodium ketone enol in addition to the methyl ester.

The 2-acetoxy-1-alkenes do not decompose when kept in contact with liquid ammonia at −34° for one hour. They do, however, react rapidly with sodium in liquid ammonia in the ratio of one mole of ester to two atoms of sodium, probably as follows



$$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{R}{\underset{|}{C}}{=}CH_2 + 2Na \longrightarrow CH_2{=}CH{-}O{-}Na + Na{-}O{-}\underset{R}{\underset{|}{C}}{=}CH_2}$$

Addition of 2-acetoxy-1-hexene to a solution of iodine in liquid ammonia also effected ester cleavage. Iodoform was the only identified product and the reaction was not further investigated.

Experimental

Reagents.—The alkenyl esters were prepared from the appropriate alkylacetylene and acid as previously described by Hennion and Nieuwland.[3] Hydrogen bromide was generated by the action of bromine on hot tetralin and was purified by passage over naphthalene followed by phosphorus pentoxide. Hydrogen chloride was obtained from sodium chloride and sulfuric acid and was dried by bubbling through sulfuric acid.

Action of Hydrogen Bromide on 2-Acetoxy-1-heptene.—A one-liter three-necked flask was equipped with a reflux condenser, a motor-driven mercury-sealed stirrer and a gas inlet tube extending to the bottom. Into the flask there was placed 117 g. (0.75 mole) of acetoxyheptene. The flask was cooled with ice and water and hydrogen bromide passed in with stirring until saturated which required about thirty minutes. The crude product was transferred to a 500-ml. round-bottomed flask provided with a 40-cm. Vigreux column and distilled. Three fractions were collected at atmospheric pressure: up to 100°, 100–140° and 140–160°. The pressure was then reduced to 23 mm. and a fraction boiling between 135–150° was collected. There was 14 g. of residue. Repeated distillation of the first three fractions yielded 38 g. (41% yield) of acetyl bromide, b. p. 80–81°, 10 g. of acetic acid, and 42 g. (49% yield) of methyl amyl ketone,[4] b. p. 145–150°. The vacuum distilled material was redistilled *in vacuo* and 15 g. of product collected between 140–150° at 23 mm. This unidentified material had the following characteristics: $n^{27}\mathrm{D}$ 1.4511; d^{27} 0.8421.

The identity of the acetyl bromide was confirmed by its action on anhydrous methanol. Methyl acetate was formed with rapid evolution of hydrogen bromide. The methyl amyl ketone yielded a semicarbazone, m. p. 122°.

Action of Hydrogen Bromide on 2-Acetoxy-1-hexene.—Hydrogen bromide was passed into 106.5 g. (0.75 mole) of acetoxyhexene at 30–32° as described above. Distillation gave 40 g. (43% yield) of acetyl bromide, 34 g. (45% yield) of methyl butyl ketone,[4] b. p. 124–127°, and 12 g. of a fraction, unidentified, b. p. 130–140° at 23 mm.; $n^{27}\mathrm{D}$ 1.4491; d^{27} 0.8465. There was 23 g. of non-distilled residue.

Action of Hydrogen Chloride on 2-(Chloroacetoxy)-1-hexene.—Hydrogen chloride was passed into 106 g. (0.6 mole) of chloroacetoxyhexene at approximately 10° as described above. Distillation to 124° at atmospheric pressure gave 40 g. of distillate. The pressure was then reduced to 20 mm. and distillation continued yielding 35 g. boiling to 90° and 35 g. boiling between 90–102°. The residue weighed 9 g. Repeated distillation yielded 25 g. of chloroacetyl chloride, b. p. 108–112°, 33 g. of methyl butyl ketone, b. p. 124–127° and 35 g. of recovered chloroacetoxyhexene, b. p. 97–102° at 20 mm.

Alcoholysis of 2-Acetoxy-1-heptene.—A solution of 0.5 g. of sodium in 12 g. of absolute methanol was treated with 47 g. (0.3 mole) of acetoxyheptene at 0°. The mixture was refluxed on a water-bath for thirty minutes and distilled. There was obtained 18 g. (81% yield) of methyl acetate, b. p. 54–57° and 28 g. (81% yield) of methyl amyl ketone, b. p. 148–155°.

A second sample of acetoxyheptene weighing 41 g. (0.263 mole) was treated with 40 g. of absolute methanol in which 1 g. of *p*-toluene sulfonic acid had been dissolved. The mixture was heated for three hours on the water-bath and distilled, yielding 15 g. of methyl acetate and 25 g. of methyl amyl ketone.

Cleavage of 2-Acetoxy-1-heptene with Sodium in Liquid Ammonia.—A mixture of 41 g. (0.263 mole) of acetoxy-

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[3] Hennion and Nieuwland, THIS JOURNAL, **56**, 1802 (1934).

[4] The product darkened upon standing unless thoroughly washed with sodium carbonate and water prior to final distillation.

heptene in 200 ml. of liquid ammonia was treated with 11.5 g. (0.5 mole) of sodium dissolved in 200 ml. of liquid ammonia. It was necessary to add 1 ml. more of the ester to effect complete decolorization of sodium. The mixture was hydrolyzed by careful addition of 250 ml. of water. The organic layer was washed twice with water, dried over calcium chloride, and distilled. Distillation was complete between 146–151° to give 23 g. (77% yield) of methyl amyl ketone. The semicarbazone melted at 122°.

Summary

Cleavage of alkenyl esters R—COO—C(R)=CH_2 with hydrogen bromide, hydrogen chloride, methanol, sodium in liquid ammonia and iodine in liquid ammonia is reported and the products described.

NOTRE DAME, INDIANA RECEIVED MARCH 9, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Anthranol-beta-*d*-glucoside[1]

BY JOHN H. GARDNER[2] AND THOMAS F. MCDONNELL

In view of the suggestion of Hauser[3] that barbaloin is a *d*-arabinoside of aloe-emodin anthranol, since it yields aloe-emodin anthrone on hydrolysis with borax solution, we have prepared anthranol-β-*d*-glucoside as the most readily obtained analogous compound and have studied its hydrolysis under a variety of conditions by the methods used previously in the study of glycosides of various mono- and dihydroxyanthraquinones.[4] It was found that anthranol-β-*d*-glucoside is hydrolyzed completely by 0.05 *N* hydrochloric acid in one hour and by 0.05 *N* potassium hydroxide in thirty minutes. Hydrolysis was 62.4% complete in one hour with 9% borax. All hydrolyses were carried out at 100°. In the acid hydrolysis, pure anthrone was recovered, but with potassium hydroxide a part of the product was oxidized to dianthrone. The hydrolysis product formed with borax was not separated from unchanged glucoside and consequently was not identified.

These results differ markedly from the behavior of barbaloin in several ways. Notably, aloin is hydrolyzed extremely slowly by hydrochloric acid yielding chiefly a red, resinous material with a small amount of aloe-emodin, an anthraquinone derivative. No evidence of the formation of aloe-emodin anthrone under these conditions has ever been found. Reasoning by analogy, it seems extremely improbable that aloin could be an arabinoside of aloe-emodin anthranol.

Experimental

Anthranol-tetraacetyl-β-*d*-glucoside.—To a solution of 0.25 g. of potassium hydroxide in 50 cc. of acetone and 25 cc. of water there were added 0.8 g. of anthrone and 1.7 g. of acetobromoglucose. The flask was closed quickly with a stopper provided with a stopcock and evacuated until the solvent boiled. The evacuated flask was swirled vigorously until an orange solution had formed and it was then allowed to stand at room temperature for five hours with occasional shaking. During this time, the solution became lemon yellow and a magma of fine needles precipitated. The reaction mixture was then diluted to 150 cc. with water and filtered. The cream colored solid was stirred into 15 cc. of methyl alcohol and filtered, leaving 0.6 g. (28%) of nearly pure anthranol-tetraacetyl-β-*d*-glucoside. After recrystallizing four times from ethyl alcohol, it formed long colorless needles, m. p. 205–205.2°.

Anal. Calcd. for $C_{28}H_{28}O_{10}$: C, 64.1; H, 5.38. Found: C, 64.0, 64.4; H, 5.54, 5.33.

Anthranol-β-*d*-glucoside.—A suspension of 0.6 g. of anthranol-tetraacetyl-β-*d*-glucoside in 75 cc. of 50% ethyl alcohol was heated to 60° and treated with 1 g. of barium hydroxide in 20 cc. of water. The mixture was maintained at 60° for fifteen minutes, with mechanical stirring. It was then cooled in ice and made slightly acid with dilute sulfuric acid. The precipitated barium sulfate was filtered out and the filtrate was concentrated under reduced pressure to 20–25 cc. The cream colored solid which separated was filtered out, crystallized from 25% ethyl alcohol and dried over sulfuric acid in a vacuum; m. p. 204–206°. Mixed with an equal quantity of the tetraacetyl glucoside, it melted at 175–187°. Its solutions in alcohol and other common solvents showed a brilliant blue fluorescence.

Anal. Calcd. for $C_{20}H_{20}O_6{\cdot}H_2O$: C, 64.1; H, 5.92. Found: C, 63.7; H, 5.33.

A sample was dried in a Pregl microdesiccator for thirty minutes at 110° in a current of dry air.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.4; H, 5.62. Found: C, 66.7; H, 5.41.

Hydrolysis Experiments.—As our supply of the glucoside was limited because of the poor yields, no attempt was

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[1] Anthracene Series. XII.

[2] This investigation was made possible by a grant to the senior author from a fund given to Washington University by the Rockefeller Foundation for research in science.

[3] Hauser, *Pharm. Acta Helv.*, **6**, 79 (1931).

[4] Gardner, McDonnell and Wiegand, THIS JOURNAL, **57**, 1074 (1935); Foster and Gardner, *ibid.*, **58**, 597 (1936); Gardner and Demaree, *ibid.*, **58**, 757 (1936).

made to determine the extent of hydrolysis for varying periods of time. Instead, one experiment with each was carried out, using 0.05 *N* hydrochloric acid, 0.05 *N* potassium hydroxide and 9% borax at 100°. With hydrochloric acid, hydrolysis was complete in one hour and with potassium hydroxide, in thirty minutes. With borax, the glucoside was hydrolyzed 62.4% in one hour. The insoluble product of acid hydrolysis was quite pure anthrone (m. p. 154–155.5°), but with potassium hydroxide, some oxidation to dianthrone occurred. The insoluble product of borax hydrolysis was not obtained free from unchanged glucoside.

Summary

Anthranol-β-*d*-glucoside has been prepared and has been found to be hydrolyzed easily in acid and alkaline media.

ST. LOUIS, MISSOURI

RECEIVED MARCH 6, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Chemistry of the Lipides of Tubercle Bacilli. XLVII. The Composition of the Avian Tubercle Bacillus Wax[1]

BY R. E. REEVES[2] AND R. J. ANDERSON

In paper X of this series Anderson and Roberts[3] described the extraction and fractionation of the lipides of the avian tubercle bacillus and it was found that the crude chloroform-soluble wax amounted to 70.7% of the total lipides and 10.79% of the dried bacterial mass. The present report deals with the properties and composition of the above mentioned wax. After the wax had been purified and saponified the cleavage products were found to consist of fatty acids, unsaponifiable matter and a water-soluble carbohydrate.

The fatty acids were a complex mixture of optically active hydroxy acids of very high molecular weight whose constitution we could not determine. None of the ordinary fatty acids could be found. The unsaponifiable matter consisted mainly of *d*-eicosanol-2 together with a small amount of *d*-octadecanol-2. The water-soluble carbohydrate was identified as trehalose.

The nature and kind of the cleavage products of the avian wax differentiate this material sharply from the previously examined wax of the human tubercle bacillus.[4] The latter product gave on saponification a mixture of fatty acids from which a hydroxy acid of high molecular weight, designated by the term "unsaponifiable wax," was isolated. The unsaponifiable matter contained the dihydric alcohol, phthiocerol, $C_{35}H_{72}O_3$,[5] while the water-soluble component was a specific polysaccharide which on hydrolysis yielded *d*-arabinose, galactose and other carbohydrates including inosite, mannose and glucosamine.

The avian wax shows considerable resemblance to the timothy bacillus wax which was recently analyzed by Pangborn and Anderson.[6] Both the avian and the timothy wax contain *d*-eicosanol-2, *d*-octadecanol-2 and trehalose together with new and previously unknown fatty acids of undetermined constitutions.

The object of the present investigation was not only to determine the chemical composition of the avian wax, which is quantitatively the most important fraction of the lipides of the avian tubercle bacillus, but also to provide sufficient quantities of the purified wax and of its cleavage products for physiological studies. The physiological experiments are being carried out by Dr. F. R. Sabin and collaborators of the Rockefeller Institute for Medical Research and will be reported independently.

Experimental Part

The crude wax isolated as described by Anderson and Roberts[3] was a non-crystalline powder of light yellow color. It was easily soluble in chloroform, ether, benzene, toluene, ligroin and ethyl acetate but it was insoluble in acetone, alcohol and methyl alcohol. The following constants were determined: m. p. 53–54°, iodine no. 7.8, saponification no. 77, $[\alpha]_D$ in $CHCl_3$ + 25.6°. A trace of phosphorus was present but sulfur, nitrogen and halogen were absent.

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[1] An abstract of this paper was read before the Division of Organic Chemistry at the meeting of the American Chemical Society, Pittsburgh, Pa., September, 1936. The data are taken from the dissertation submitted by Richard E. Reeves to the Faculty of the Graduate School, Yale University, 1936, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The present report is a part of a coöperative investigation on tuberculosis; it has been supported partly by funds provided by the Research Committee of the National Tuberculosis Association.

[2] Holder of a National Tuberculosis Association Graduate Student Fellowship at Yale University, 1934–1936.

[3] R. J. Anderson and E. G. Roberts, *J. Biol. Chem.*, **85**, 509 (1930).

[4] R. J. Anderson, *ibid.*, **83**, 505 (1929).

[5] F. H. Stodola and R. J. Anderson, *ibid.*, **114**, 467 (1936).

[6] M. C. Pangborn and R. J. Anderson, THIS JOURNAL, **58**, 10 (1936).

Purification of the Wax.—For purification 170 g. of the wax was precipitated from solution in chloroform or ether by adding methyl alcohol and cooling. The wax separated as a white, granular powder. The optical rotation increased slowly during purification until the maximum value of +38.6° was attained after forty precipitations. The yield of the purified wax, designated Fraction I, was 69.6 g. The substance had the following properties, m. p. 54–55°, iodine no. 4.5, $[\alpha]_D$ in $CHCl_3$ +38.6°. It contained the merest trace of phosphorus. On combustion it gave C, 75.38, H, 12.14. When titrated in ether–alcohol solution the wax was found to be essentially neutral.

The material contained in the mother liquors was recovered as follows. (a) The mother liquors from the first ten precipitations were concentrated to dryness. The residue which contained most of the coloring matter of the original wax formed a yellowish solid and it weighed 35.1 g. This fraction was set aside and was not examined further. (b) The mother liquors from the subsequent precipitations were concentrated to dryness. The residue was dissolved in chloroform and precipitated by adding methyl alcohol and cooling. The nearly white powder which was obtained weighed 62.2 g. and was designated Fraction II. It had the following properties: m. p. 53–55°; iodine no. 8.7; $[\alpha]_D$ in $CHCl_3$ +17.7°. Except for a lower optical rotation and a somewhat greater solubility Fraction II was very similar to Fraction I.

Since neither fraction could be obtained in crystalline form they were saponified and the cleavage products were separated.

Saponification of the Wax.—The purified wax, Fraction I, was saponified in two lots; in each case 25 g. of the wax was refluxed for ten hours on a water-bath with 500 cc. of 1.6% alcoholic potassium hydroxide. Fraction II was also saponified in two lots using a corresponding quantity of alcoholic potassium hydroxide. The wax melted in the boiling alcohol and as the saponification proceeded the oil was replaced gradually by a brittle cake on the bottom of the flask. The material was never completely in solution.

Separation of the Cleavage Products. The Alcohol-Insoluble Fraction "A."—The hot alcoholic solution was decanted from the insoluble cake and the flask was rinsed several times with hot alcohol. The residue in the flask was extracted with hot benzene and the material obtained on evaporation of the solvent was added to the alcoholic solution. The alcohol and benzene insoluble fraction was soluble in water and was reserved for the isolation of trehalose as will be described later.

Alcohol-Insoluble Potassium Soaps. Fraction "B."—The alcoholic solution containing the potassium salts of fatty acids, unsaponifiable matter, etc., deposited on cooling a large amount of a white precipitate which was found to consist of the potassium salts of high molecular weight fatty acids. The precipitate was filtered off, washed with cold alcohol and dried.

Fatty Acids from the Alcohol-Soluble Potassium Soaps. Fraction "C."—The filtrate from the alcohol-insoluble potassium salts was freed from excess of potassium hydroxide by means of carbon dioxide. The potassium carbonate was filtered off, washed with alcohol and discarded. The filtrate and washings were concentrated to a volume of about 200 cc. and the hot solution was mixed with a hot alcoholic solution of lead acetate. The precipitate which separated on cooling was filtered off, washed with alcohol and decomposed in the usual manner, yielding a small amount of fatty acid.

The alcoholic filtrate from the lead salt was concentrated *in vacuo* to dryness and the residue was mixed with water and extracted with ether. The aqueous solution was reserved and examined for glycerol as will be described below.

The ethereal solution was washed first with dilute acetic acid for the removal of any lead which might be present, and then with water until the washings were neutral, after which it was twice extracted with dilute potassium hydroxide. The ethereal solution was reserved for the isolation of unsaponifiable or neutral material. The alkaline extract was acidified and extracted with ether. The ethereal extract yielded on evaporation a small amount of fatty acids which was combined with the acids obtained from the lead salts.

The Unsaponifiable or Neutral Material. Fraction "D."—The ethereal solution, after the alkaline extraction mentioned above, was washed with water, treated with norite, filtered and the ether was distilled off. The residue, which was a white crystalline solid, was found to consist of two optically active higher alcohols as will be described later.

Examination for Glycerol.—The aqueous solution which had been reserved for the examination for glycerol was evaporated to dryness *in vacuo*. The residue was extracted with warm pyridine, filtered and the pyridine was evaporated *in vacuo*. In no case was any weighable residue obtained and we conclude therefore that the wax did not contain any glycerol. Furthermore, no reducing sugar could be detected in the pyridine-insoluble salt residue.

A summary of the cleavage products of the wax fractions is presented in Table I.

TABLE I

CLEAVAGE PRODUCTS OF THE AVIAN WAX

	Purified wax		Wax fraction II
Wax saponified, g.	25.0	25.0	62.2
Carbohydrate, Fraction "A," %	11.3	13.3	5.6
Alcohol-insoluble soaps, Fraction "B," %	80.0	82.0	84.8
Acid from alcohol-soluble soaps, Fraction "C," %	2.2	2.6	6.8
Neutral material, Fraction "D," %	10.8	9.1	9.0
Glycerol	None	None	None

Examination of the Cleavage Products

Isolation and Identification of Trehalose.—The alcohol insoluble Fraction "A" was dissolved in water and the solution was neutralized with acetic acid. The solution was filtered from a slight amount of insoluble material, concentrated *in vacuo* to a small volume, and neutral lead acetate solution added until no further precipitate formed. The slight precipitate was filtered off and discarded. A carbohydrate was isolated from the filtrate by means of basic lead acetate and ammonia in the usual manner. The crude carbohydrate, which was obtained as a white powder, gave no pentose reactions and no reduction with Fehling's solution until after it had been boiled for some time with dilute acid.

One gram of the substance was acetylated and yielded 1.95 g. of the acetyl derivative. After two crystallizations as described by Pangborn and Anderson[6] the colorless, needle-shaped crystals weighed 1.2 g. and after being heated at 60° *in vacuo* for several hours melted at 97–98°. In chloroform solution $[\alpha]_D$ was +163.7°. On saponification 70.6% of acetic acid was liberated. Trehalose octaacetate requires 70.8% of acetic acid.

The acetyl derivative, 6.5 g., prepared as above, was saponified and the free trehalose was isolated and crystallized from 80% alcohol. Large, colorless, prismatic crystals were obtained which weighed 1.7 g. and melted at 98°, $[\alpha]_D$ in water +178°. On drying at 78° *in vacuo* the crystals lost 9.85% in weight. Calcd. for $C_{12}H_{22}O_{11}\cdot 2H_2O$: H_2O, 9.52.

These data complete the identification of the carbohydrate as trehalose.

Examination of the Acids from the Alcohol-Insoluble Potassium Salts. Fraction "B."—The alcohol-insoluble Fraction "B" was found to consist of potassium salts of fatty acids of high molecular weight. The separation of the free acids by fractional precipitation or by fractionation of the acetyl derivative was difficult and incomplete. A more rapid and satisfactory separation into two distinct fractions was effected by means of the difference in solubility of the potassium salts between ligroin and methyl alcohol. The potassium salts were easily soluble in ligroin and when the ligroin solution was shaken with methyl alcohol two layers separated. The alcoholic solution contained the salt of an acid having a molecular weight of about 500, Fraction BI, while the ligroin solution contained the salt of an acid having a molecular weight of about 1300, Fraction BII. By repeating the procedure several times with each fraction two acids were obtained in about equal amounts whose properties remained essentially unchanged by further attempts at purification. The potassium salt of the acid having the lower molecular weight although insoluble in pure methyl alcohol was easily soluble in methyl alcohol containing ligroin.

An adequate purification of these wax acids was impossible by present available methods. The acids do not crystallize but separate from solvents in the form of colorless, globular particles; hence criteria of purity are entirely lacking. The analytical values for carbon and hydrogen and the molecular weights as determined by titration do not correspond to any definite empirical formula. The reason may depend upon lactone formation.

The analyses of the acids and of their derivatives indicate that the acids contain more than 2 atoms of oxygen but we have been unable to demonstrate conclusively that a third oxygen atom is present as a hydroxyl group although the methyl esters show some active hydrogen[7] and the free acids on acetylation yield products which are partly acetylated. The ratio of C:H is somewhat less than 1:2 but the acids show a low iodine number and on treatment with bromine they yield anomalous bromine derivatives, bromine is absorbed and is also slowly substituted with liberation of hydrobromic acid.

The free acids were prepared from the potassium salts in the usual manner and purified by precipitation from ethereal solution by the addition of alcohol. The acids were easily soluble in ether, chloroform, ligroin and benzene but insoluble in alcohol or acetone. Dr. F. R. Sabin examined these acids and found that they were acid-fast.

In general the properties of the avian wax acids resemble those of the analogous acids encountered in the wax from human tubercle bacillus[4] and in the timothy bacillus wax[6] but they are not identical.

The complete elucidation of the composition and structure of these interesting but very complex wax acids must be left for future investigations. For the present we record the observed properties of the free acids and of some of their derivatives in Table II.

TABLE II

PROPERTIES OF THE AVIAN WAX ACIDS

	Fraction BI	Fraction BII
Free acid, m. p., °C.	69–70	60–61
$[\alpha]_D$ in $CHCl_3$	+5.6°	+5.5°
Analysis	C, 78.99; H, 12.78	C, 82.46; H, 13.49
Mol. wt. by titration	501–520	1280–1300
Approximate formula	$C_{38}H_{74}O_3$	$C_{88}H_{174}O_3$
Acetyl derivative, m. p., °C.	54–55	48–57
Methyl ester, m. p., °C.	54–55	49–50
Active hydrogen of ester,[7] %	0.92	0.82
Bromo derivative	m. p. 47–49° Br. 22.4%	m. p. 43–49° Br. 22.9%
Iodine number (Hanus)	6.5	5.5

Fraction C.—The acids obtained from Fraction C represented only a small percentage of the total acids. They were semi-solid, had low iodine numbers and were obviously a mixture from which no pure substance could be isolated, nor could any of the usual fatty acids be found.

The Neutral Material. Fraction D. Isolation of *d*-Eicosanol-2.—The neutral material was found to consist largely of *d*-eicosanol-2 but a small amount of *d*-octadecanol-2 was also present. The isolation of *d*-eicosanol-2 was accomplished readily by crystallization. After the crude neutral material had been crystallized three times from ethyl acetate and twice from methyl alcohol, colorless prismatic crystals were obtained which melted at 62–63° and gave no depression when mixed with an authentic specimen of *d*-eicosanol-2; $[\alpha]_D$ in ether +6.79°.

Anal. Calcd. for $C_{20}H_{42}O$(298): C, 80.55; H, 14.18. Found: C, 80.54; H, 14.25; mol. wt. (Rast), 294.

The 3,5-dinitrobenzoate was prepared and recrystallized from alcohol. Colorless, needle-shaped crystals were obtained which melted at 77.5–78°; $[\alpha]_D$ in $CHCl_3$ +23.4°.

Anal. Calcd. for $C_{27}H_{44}O_6N_2$(492): C, 65.82; H, 9.01. Found: C, 65.62; H, 8.91.

Oxidation of the alcohol by the procedure employed by Pangborn and Anderson[6] yielded eicosanone-2, colorless thin plates, m. p. 60–61°. The melting point was not depressed when the ketone was mixed with a sample of synthetic eicosanone-2.

Anal. Calcd. for $C_{20}H_{40}O$(296): C, 80.99; H, 13.61. Found: C, 80.73; H, 13.44.

The semicarbazone was prepared and crystallized from alcohol. Colorless, prismatic crystals were obtained which

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(7) T. Zerewitinoff, *Ber.*, **40**, 2023 (1907).

melted at 130–131°. The melting point was not depressed when the semicarbazone was mixed with the semicarbazone of eicosanone-2.

Isolation of *d*-Octadecanol-2.—The material recovered from the mother liquor from *d*-eicosanol-2 yielded very small quantities of *d*-octadecanol-2. A portion of this material, 0.9 g., was converted into the phenylurethan. The latter after more than 100 recrystallizations yielded 60 mg. of needle-shaped crystals which had the correct melting point, 76–76.5°, of the phenylurethan of *d*-octadecanol-2. A mixed melting point with an authentic specimen gave no depression. However, this method of purification was too laborious and the yield too small.

Another portion of the crude material, 2.53 g., was first fractionated by distillation through a modified Widmer column into 3 fractions. The first fraction, 0.73 g., which distilled at 170–190° and 3 mm. pressure, was converted into the 3,5-dinitrobenzoate. The product, after treatment with norite, was recrystallized from alcohol until the melting point was constant at 71–72°. The colorless needle-shaped crystals weighed 0.45 g.; $[\alpha]_D$ in $CHCl_3$ $+25.3°$.

Anal. Calcd. for $C_{25}H_{40}O_6N_2$(464): C, 64.61; H, 8.68. Found: C, 64.78; H, 8.56.

The dinitrobenzoate, 392 mg., was saponified by refluxing with 4% alcoholic potassium hydroxide. After the alcohol had been isolated and recrystallized four times from methyl alcohol, 197 mg. of colorless needles was obtained. The crystals melted at 53–54° and there was no depression when mixed with *d*-octadecanol-2; $[\alpha]_D$ in $CHCl_3$ $+4.84°$.

Anal. Calcd. for $C_{18}H_{38}O$(270): C, 79.91; H, 14.17. Found: C, 80.15; H, 13.98; mol. wt. (Rast), 271.

The octadecanol-2, 88 mg., was oxidized to the ketone and the latter was recrystallized three times as described by Pangborn and Anderson.[6] The yield was 32 mg. of colorless, plate-shaped crystals. The ketone melted at 50–51° and there was no depression when mixed with a sample of synthetic octadecanone-2.

Summary

1. The chloroform-soluble wax of the avian tubercle bacillus has been purified, saponified and the cleavage products investigated.

2. The principal constituents of the wax are hydroxy fatty acids of very high molecular weight. The acids were acid-fast and were optically active. None of the usual fatty acids were found.

3. The unsaponifiable matter of the wax consisted of *d*-eicosanol-2, $C_{20}H_{42}O$, together with a small amount of *d*-octadecanol-2, $C_{18}H_{38}O$.

4. The water-soluble component of the wax liberated on saponification was identified as the disaccharide trehalose, $C_{12}H_{22}O_{11}$.

5. Glycerol could not be detected among the cleavage products.

NEW HAVEN, CONN. RECEIVED MARCH 8, 1937

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

The Oxidation of Substituted Phenols. The Effect of Iodine in the Ortho and Para Positions

BY G. H. WOOLLETT, F. M. DAVIS, C. N. JONES AND MARY NEILL

Upon oxidation 2,6-dimethoxyphenol is converted almost quantitatively into cedriret (3,5,3′,5′-tetramethoxydiphenoquinone-4,4′)[1] while similar phenols such as 2,6-dimethylphenol[2] and 2,6-diacetamidophenol[3] yield 70% or more of dinuclear quinones. These are highly colored conspicuously crystalline sparingly soluble compounds whose structure has been verified amply. The reaction is commonly cited as an example of steric hindrance. Carboxyl, chlorine, bromine,[4] hydroxyl, methoxyl[2] and methyl para to the hydroxyl prevent the reaction.

Another group of substances often confused with the true dinuclear quinones is the highly colored resinoids obtained by the action of iodine and alkali on phenols having ortho and para positions unsubstituted. One of these (Lautemann's Red), obtained from common phenol, was said to be 3,5,3′,5′-tetraiododiphenoquinone-4,4′, by Kammerer and Benzinger[5] shortly after the report on the structure of cedriret by Hoffman, the similarity in color no doubt being the cause of the mistake. The analogous product from thymol[5,6] (aristol) was also thought to be a dinuclear quinone. Later investigators[7–10] agree that Lautemann's Red and aristol are amorphous and have high molecular weights, although it has been sug-

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(1) A. W. Hoffman, *Ber.*, **11**, 329 (1878).

(2) Auwers and others, *ibid.*, **38**, 226 (1905); **57**, 1270 (1924).

(3) Fromm and Ebert, *J. prakt. Chem.*, **108**, 75 (1924).

(4) Hunter and Levine, THIS JOURNAL, **48**, 1608 (1926).

(5) Kammerer and Benzinger, *Ber.*, **11**, 557 (1878).

(6) Messinger and Vortmann, *ibid.*, **22**, 2314 (1889); Vortmann, *ibid.*, **56B**, 234 (1923).

(7) Bougault, *Compt. rend.*, **146**, 1404 (1908).

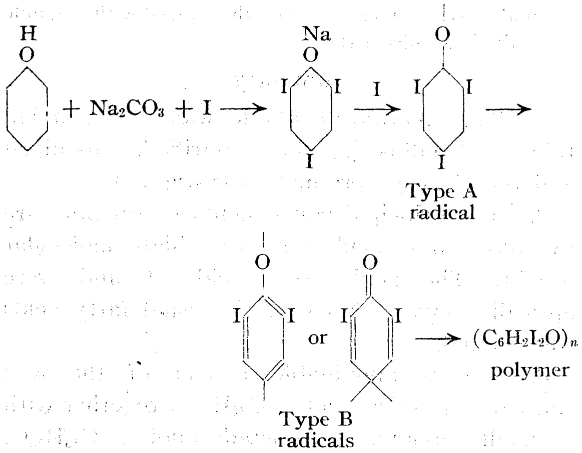
(8) Carswell, *Chem. News*, **68**, 87, 99, 131, 153, 166, 181 (1893).

(9) Hunter and Woollett, THIS JOURNAL, **43**, 131, 135 (1921).

(10) Woollett and others, *ibid.*, (a) **38**, 2474 (1916); (b) **43**, 553 (1921); (c) **52**, 4018 (1930); (d) **55**, 2909 (1933).

gested recently that aristol is a dimer of diiododithymoquinone.[11]

A mechanism suggested by Hunter[9,12] for the formation of Lautemann's Red is shown by the series of reactions



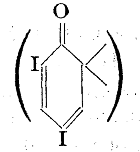
If this is correct some true dinuclear quinone should be formed, the amount depending upon the relative stability of the quinoid form of the type B radical. Showing that the formation of cedriret and the colored resinoids do, after all, have something in common, Hunter and Morse[13] have obtained a 5.6% yield of a true tetraiododiphenoquinone by rapid oxidation of potassium triiodophenolate, the remainder being largely Lautemann's Red. Additional work done in this Laboratory on the role of iodine in the two types of reactions is presented here.

The preparation of tetraiododiphenoquinone from triiodophenol has been repeated and confirmed. Since iodine in the para position in triiodophenol does not prevent the formation of dinuclear quinone, it would be expected that some of this quinone would be made during the preparation of Lautemann's Red in the usual way. This has been shown to occur to the extent of 2.1%.

The largest yield of the quinone would be expected to result from the oxidation of 2,6-diiodophenol. This has proved to be approximately 31%.

Thus the "pro" effect of iodine in the 2,6-position in causing the cedriret reaction may be represented by the figure 31 and the "con" effect of iodine in the para position by the decrease from 31 to 5.3 or 83%. The formation of tetraiododiphenoquinone from 2,6-diiodophenol also shows that the iodine atoms occupy the 3,5- and 3′,5′-positions relative to the bonds between the rings.

By way of checking the effect of iodine it was found that oxidation of 2,6-dibenzamidophenol and 2,6-dibenzamido-4-iodophenol yields 84 and 11.3% of 3,5,3′,5′-tetrabenzamidodiphenoquinone-4,4′, respectively, thus showing a "pro" figure of 80 for benzamido and a "con" of 86% (84 to 11.3) for para iodine.

As the diphenoquinones isolated are para quinones and as it has been shown previously[14] that either ortho or para iodine may be removed in the formation of resinoids but that the resinoids from para cresol[10d] and 2,4-dimethylphenol in which the iodine removed must be from the ortho position are practically colorless it seems probable that the ortho quinoid form of the diiodo type B radical  is not formed.

Experimental

2,6-Diiodo-4-nitrophenol.—Para nitrophenol was iodinated in hot sodium carbonate solution with an excess of iodine–potassium iodide solution. The conditions are not critical.

2,6-Diiodo-4-aminophenol.—A modification of the general method of Hodgson and Kershaw[15] was used. To a hot solution of 50 g. of diiodonitrophenol and 100 g. of sodium carbonate in 1200 cc. of water 80 g. of sodium hydrosulfite was added gradually during energetic stirring. Pure 2,6-diiodo-4-aminophenol, m. p. 170°, separated in 86% yield. Raiford, Taft and Lankelma[16] give 169–171°.

2,6-Diiodophenol.—A cooled solution of 10 g. of diiodoaminophenol in 250 cc. of alcohol and 5 cc. of sulfuric acid was treated gradually with the calculated amount (22 cc.) of *N* sodium nitrite, then refluxed for one hour, cooled, made slightly alkaline with ammonium hydroxide containing a little sodium bisulfite, water added and the phenol extracted with ether; yield 5 g. (52%). This was purified by steam distillation, precipitation from alcoholic solution by a large amount of ice water, and finally from hot glacial acetic acid; white needles, m. p. 67.2°.

Oxidation of 2,6-Diiodophenol and Isolation of 3,5,3′,5′-Tetraiodo-4,4′-dihydroxydiphenyl.—One gram of diiodophenol was dissolved in 10 cc. of water and 1.5 cc. of 2 *N* potassium hydroxide, cooled and poured into a cooled solution of 10 g. of chromium trioxide in 10 cc. of water. The mixture was shaken for ten minutes and filtered by suction. Average weight of red precipitate at this time was 0.775 g.

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[11] Bordeianu, *Arch. Pharm.*, **272**, 8 (1934).

[12] Hunter and Seyfried, This Journal, **43**, 151 (1921).

[13] Hunter and Morse, *ibid.*, **55**, 3701 (1933).

[14] Hunter and Joyce, *ibid.*, **39**, 2640 (1917).

[15] Hodgson and Kershaw, *J. Chem. Soc.*, 2703 (1928).

[16] Raiford, Taft and Lankelma, This Journal, **46**, 2057 (1924).

The red mixture was wet with alcohol and treated with a solution of 1 g. of hydrazine sulfate in 20 cc. of 2 *N* potassium hydroxide, filtered, treated with Norite, refiltered, and precipitated with acetic acid: average yield of white microscopic needles, 0.308 g. (31%). After recrystallizing twice from hot acetone by adding glacial acetic acid it melted with decomposition at 284° if the melting point tubes were inserted in the bath after it had reached 250°. A lower melting point and more decomposition resulted from the usual treatment.

Anal. (Carius). Calcd. for $C_{12}H_6I_4O_2$: I, 73.61; mol. wt. 689.73. Found: I, 73.50, 73.43; mol. wt. (Rast), 662, 640.

Other products of oxidation of 2,6-diiodophenol as found in samples from 1 g. of phenol: by steam distillation, *m*-diiodoquinone, 0.06 g., yellow platelets from hot alcohol, m. p. 175–176°. Amorphous product, 0.067 g.: insoluble in alkali after reduction and when reoxidized by lead dioxide in carbon bisulfide and precipitated by heptane became a red powder. This is evidently Lautemann's Red. A sticky yellow substance soluble in alcohol, 0.338 g.

Tetraiododiphenol from Phenol.—Lautemann's Red was made from 15.7 g. of phenol by treating with sodium carbonate and iodine in the usual way.[5] After thorough washing the wet product was reduced by treating with 320 cc. of 2 *N* potassium hydroxide, 600 cc. of water and 11 g. of hydrazine sulfate. The bleached material was filtered and extracted twice with *N* potassium hydroxide and filtrate and washings acidified. The white precipitate weighed 1.928 g. and consisted mainly of triiodophenol and tetraiododiphenol. Triiodophenol was removed by treating this, dissolved in 3 cc. of 2 *N* potassium hydroxide and 40 cc. of water, with 14 g. of potassium ferricyanide in 60 cc. of water. The red precipitate was filtered, washed and reduced as before using 1.5 g. of hydrazine sulfate, 20 cc. of alkali and 50 cc. of water. The filtrate and washings from this, after warming with Norite, filtration and acidification, yielded 1.20 g. (2.1%) of white microscopic needles which, after recrystallizing twice from acetone and glacial acetic acid, melted at 283° and showed no change in m. p. when mixed with an equal quantity of tetraiododiphenol from 2,6-diiodophenol.

Tetraiododiphenol from Triiodophenol.—The preparation was made according to the directions of Hunter and Morse[13] except that it was crystallized from acetone–acetic acid, m. p. (pre-heated bath) 283°. When mixed with an equal quantity of the analogous product from 2,6-diiodophenol it also melted at 283°.

Oxidation of 3,5,3′,5′-Tetraiodo-4,4′-dihydroxydiphenyl.—Samples from the three sources were oxidized in glacial acetic acid or ethyl acetate by chromium trioxide or ferric chloride; however, oxidation in ethyl acetate by chromium trioxide gave best crystals. All samples behaved identically producing microscopic green needles with metallic luster and red streak and which decomposed without melting. The product apparently may be reduced and reoxidized indefinitely. No satisfactory solvent was found.

2,6-Dibenzamidophenyl Benzoate.—Forty-two grams of sodium hydrosulfite was added in 10-g. portions with energetic shaking to a hot solution of 2,6-dinitrophenol (5 g.) in 650 cc. of water. The faintly colored solution was cooled and 70 cc. of 40% sodium hydroxide added, followed by 25 cc. of benzoyl chloride. Eleven grams (93%) of the tribenzoyl compound separated and after recrystallization twice from glacial acetic acid melted at 220°.

2,6-Dibenzamidophenol.—Fromm and Ebert's[8] method was used, giving light yellow needles of m. p. 179–180°.

Oxidation of 2,6-Dibenzamidophenol.—Sodium nitrite, periodic acid and permanganate produced the quinone in glacial acetic acid. Nitrite, however, gave the cleanest product. Samples of 0.1 to 0.3 g. were dissolved in from 18 to 50 cc. of glacial acetic acid and treated with 0.3 cc. of 20% sodium nitrite solution per 0.1 g. of phenol. After fifteen minutes the quinone was filtered off, dissolved in 150 cc. of chloroform for each 0.1 g. of quinone and precipitated by adding 2.5 volumes of alcohol: average yield from 18 samples, 84% of 3,5,3′,5′-tetrabenzamidodiphenoquinone-4,4′; greenish black microscopic needles which decomposed without melting and which have metallic luster and purple streak. Chloroform solutions were deep permanganate color.

Anal. Calcd. for $C_{40}H_{28}N_4O_6$: N, 8.45; O, 4.84; mol. wt., 660. Calcd. for $C_{20}H_{14}N_2O_4$: N, 8.09; O, 9.25; mol. wt., 346. Found: N (Dumas), 8.79, 8.79; quinoid O (hydrazine) 4.74, 5.08, 4.87, 5.05; mol. wt. (Rast), 696, 557.

2,6-Dinitro-4-iodophenol.—This was made from isopicramic acid and also by iodination of 2,6-dinitrophenol in glacial acetic acid by iodine monochloride. Both melted at 113°.

2,6-Dibenzamido-4-iodophenylbenzoate.—Five grams of dinitroiodophenol and 10 g. of sodium bicarbonate were dissolved in 300 cc. of water to which 25 g. of sodium hydrosulfite was added in portions with energetic shaking. As ordinary Schotten–Baumann procedure removed iodine the mixture was made alkaline with sodium bicarbonate and the amine extracted with ether. The ether solution was filtered and to it added 10 cc. of pyridine and 6 cc. of benzoyl chloride. After the voluminous precipitate had formed 200 cc. of alcohol was added and 4.6 g. (50%) of the tribenzoyl compound filtered off. After recrystallization from hot glacial acetic acid colorless needles melting at 253–254° (dec.) were obtained.

Anal. (Carius). Calcd. for $C_{27}H_{19}N_2O_4I$: I, 22.59. Found: I, 22.75, 22.24.

2,6-Dibenzamido-4-iodophenol.—Four grams of the tribenzoyl compound was dissolved in a mixture of 320 cc. of alcohol and 13 cc. of 10% sodium hydroxide. The yellow solution was diluted with 500 cc. of water and acidified, yielding 3.3 g. (99%) of colorless microscopic needles which after recrystallization from hot acetic acid melted with decomposition at 232°.

Anal. (Carius). Calcd. for $C_{20}H_{15}N_2O_3I$: I, 27.75. Found: I, 27.83, 28.07, 27.64, 28.14.

Oxidation of 2,6-Dibenzamidophenol.—A solution made by mixing 10 cc. of 10% sodium hydroxide with 6 g. of the phenol and adding 1 liter of water was poured with vigorous stirring into a solution containing 40 g. of chromium trioxide and 1200 cc. of water. The red precipitate was digested with 800 cc. of alcohol to dissolve the main product of the reaction—presumably *m*-dibenzamidobenzoquinone. The portion insoluble in alcohol was dissolved in 500 cc. of chloroform and precipitated with 1000 cc. of alcohol. The yield was 0.485 g. (11.3%) of greenish black microscopic needle-shaped crystals having metallic luster and purple streak and which appeared to be identical with those obtained from 2,6-dibenzamidophenol.

Anal. (Kjeldahl). Calcd. for $C_{40}H_{28}N_4O_6$: N, 8.49; quinoid O, 4.84. Found: N, 8.31; quinoid O (hydrazine), 5.22, 5.24.

The alkali salt of the hydroquinone formed by reduction of quinone from either source by hydrazine is yellow. Its yellow solution on acidification yields the colorless hydroquinone which rapidly becomes purple in the air. Reoxidized quinone from the above preparation contained 8.92% N which indicates some saponification of benzamido groups has occurred.

Summary

1. Iodine in the 2,6-position in phenols is about 37% as efficient as benzamido in favoring the cedriret reaction.

2. Placing iodine in the 4-position in 2,6-diiodophenol or 2,6-dibenzamidophenol does not prevent the cedriret reaction but decreases the yield by 83–86%.

3. The positions of the iodine atoms in the tetraiododiphenoquinone have been determined and 2,6-dibenzamido-4-iodophenol and 3,5,3′,5′-tetrabenzamidodiphenoquinone-4,4′ have been prepared.

University, Miss. Received March 3, 1937

[Contribution No. 175 from the Experimental Station of E. I. du Pont de Nemours and Company]

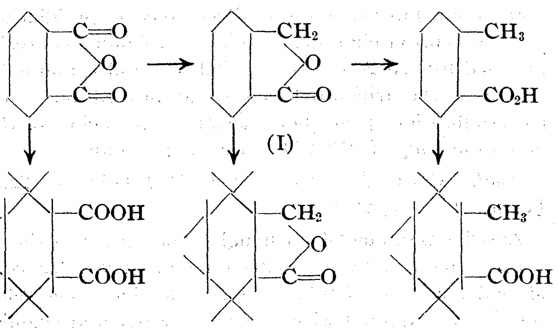
Phthalide. I. The Hydrogenation of Phthalic Anhydride

By Paul R. Austin, E. W. Bousquet and Wilbur A. Lazier

Phthalic anhydride has been hydrogenated over nickel[1] and platinum[2] catalysts by a number of investigators, all of whom note the formation of phthalide (I) accompanied by varying amounts of toluic acid as well as ring-hydrogenated derivatives of the components of the reaction mixture (Chart I).

Chart I

Hydrogenation of Phthalic Anhydride



The complexity of the reaction may be illustrated by the recent work of Adkins, Wojcik and Covert[1d] who carried out the hydrogenation with nickel and isolated about equal amounts of phthalide, *o*-toluic acid and hexahydro-*o*-toluic acid. It was thought worth while to investigate further the optimum conditions for the catalytic synthesis of phthalide. Since early trials showed the presence of a solvent to be essential to high conversions, this factor was given primary consideration.

With nickel-on-kieselguhr catalyst yields of phthalide above 80% of the theoretical were realized using ethanol as the reaction medium. This process was carried out at 150–160°, a temperature at which the phthalic anhydride is converted readily to ethyl hydrogen phthalate and one might expect that the hydrogenation of this aromatic ester would be limited to the nucleus[1d] or inhibited completely by the action of the acid on the nickel catalyst.[3] The formation of phthalide which occurs in the presence of alcohol, leads us to postulate the hydrogenation of the tautomeric form of ethyl hydrogen phthalate (II), the course of the reduction proceeding by hydrogenolysis[4] in accordance with the following scheme (Chart II).

Furthermore, the closely related ester, *pseudo*-ethyl phthalaldehydate (III), hydrogenated smoothly to phthalide and *o*-toluic acid as predicted by this hypothesis. It is interesting to note that ester solvents, such as ethyl acetate, ethyl butyrate and butyl acetate may be employed satisfactorily in this process.

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[1] (a) Godchot, *Bull. soc. chim.*, [4] **1**, 829 (1907); (b) Eijkman, *Chem. Weekblad*, **4**, 191 (1907); (c) Lucius and Bruning, German Patent 368,414 (1923), *Friedl.*, **14**, 454; (d) Adkins, Wojcik and Covert, This Journal, **55**, 1669 (1933).

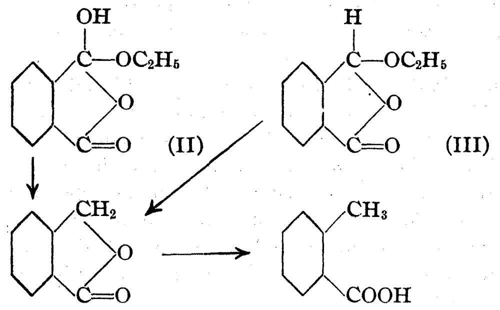
[2] Willstätter and Jaquet, *Ber.*, **51**, 767 (1918); Vavon and Peignier, *Bull. soc. chim.*, [4] **45**, 297 (1929).

[3] Covert, Connor and Adkins, This Journal, **54**, 1661 (1932).

[4] Connor and Adkins, *ibid.*, **54**, 4678 (1932).

CHART II

HYDROGENATION OF ETHYL HYDROGEN PHTHALATE AND *pseudo*-ETHYL PHTHALALDEHYDATE



The use of Raney nickel catalyst in alcohol gave a relatively high conversion to phthalide and a low proportion of toluic acid, but the catalyst was found to promote considerable nuclear saturation. The effect of temperature on the distribution of the reaction products was rather marked. Hydrogenation in alcohol solution with nickel catalyst at 160° gave about 20% of toluic acid at the expense of a portion of the phthalide, while at 150° only 10% of toluic acid was obtained, and the yield of phthalide was above 80%. At 140° the hydrogen absorption was very slow. The conversion to hexahydrophthalide was little affected by the temperature in this range but, as indicated above, was largely dependent on the type of catalyst employed. Pressures varying from 700–2000 lb./sq. in. (47–133 atm.) were about equally satisfactory in all of the hydrogenations using nickel.

Nuclear saturation and relatively high conversions to *o*-toluic acid are inherent disadvantages in the hydrogenation of phthalic anhydride with nickel, and to obviate these factors other types of catalysts were investigated. Copper chromite was the most effective in accomplishing this purpose. Benzene was found to be a suitable solvent, and hydrogenation carried out at 270° under 3000 pounds per sq. in. (200 atm.) of hydrogen pressure gave phthalide in a yield of 82.5%, while the conversion to *o*-toluic acid was about 10%. Alcohols were not useful as solvents for hydrogenations with copper chromite; for example, copper–barium chromite catalyst with ethanol and phthalic anhydride gave toluene, xylene and diethyl phthalate, but no phthalide. In hydrogenating phthalic anhydride in the absence of a solvent, copper–barium chromite and copper chromite catalysts gave 10 and 56% of phthalide, respectively.

By applying the hydrogenation technique to phthalide and some of its derivatives, a series of interesting compounds has been prepared. Thus Raney nickel catalyst with phthalide itself gave hexahydro-phthalide (82.5% conversion), 5-nitrophthalide was reduced over nickel-on-

TABLE I

HYDROGENATION OF PHTHALIC ANHYDRIDE AND PHTHALIDE DERIVATIVES

Run no.	Material hydrogenated	Grams	Catalyst	Grams	Solvent	Grams	Time, hrs.	Temp., °C.	Mean pressure, lb./sq. in.	Phthalide, %	*o*-Toluic acid, %
1	Phthalic anhydride	100	Ni-on-Kies.	11	Ethyl butyrate	176	1.0	170	1500	66.3	16.3
2	Phthalic anhydride	100	Ni-on-Kies.	10	Butyl acetate	100	2.5	160	2000	70.8	21.8
3	Phthalic anhydride	100	Ni-on-Kies.	10	Ethyl acetate	100	1.5	160	700	69.5	19.5
4	Phthalic anhydride	148	Ni-on-Kies.	15	Abs. ethanol	46	2.0	160	1500	72.4	16.5
5	Phthalic anhydride	148	Ni-on-Kies.	12	Methanol	32	4.75	150	1000	83.0[a]	10.8
6	Phthalic anhydride	148	Ni-on-Kies.	12	95% ethanol	50	4.0	150	1200	81.0[a]	12.5
7	Phthalic anhydride	148	Raney Ni	15	Abs. ethanol	50	4.0	160	2500	73.0[b]	10.3
8	Ethyl hydrogen phthalate	150	Ni-on-Kies.	11	None	..	5.25	150	1200	77.0[a]	12.7
9	Phthalic anhydride	150	Cu–Cr	12	None	..	5.0	270	3000	55.8[c]	3.6
10	Phthalic anhydride	150	Cu–Ba–Cr	12	None	..	8.0	270	3500	14.6[d]	8.7
11	Phthalic anhydride	8000	Cu–Cr	800	Benzene	8000	6.0	260	3000	82.5	9.8
12	*pseudo*-Ethyl phthalaldehydate	45	Ni-on-Kies.	3.6	95% ethanol	25	3.0	150	1200	50.4[e]	43.5
13	Phthalide	200	Raney Ni	20	None	..	2.0	140	2000	Hexahydrophthalide, 82.5%[f]	
14	5-Nitrophthalide	1000	Ni-on-Kies.	50	Abs. ethanol	3500	1.0	150	1500	5-Aminophthalide, 85%[g]	
15	Sodium-α-hydroxy-*o*-toluate	195	Ni-on-Kies.	20	Water	300	6.5	110	1500	*o*-Toluic acid, 80%	

[a] About 3–4% of hexahydrophthalide also was obtained. [b] Seven per cent. of hexahydrophthalide was also isolated. [c] Phthalic acid 33.4% also was obtained. [d] Phthalic acid, 64.7%, predominated. [e] *pseudo*-Ethyl phthalaldehydate was prepared according to the procedure outlined by Meyer [*Monatsh.*, **25**, 491 (1904)]; it melted at 66°. [f] *o*-Toluic acid (1.0%) and hexahydro-*o*-toluic acid (6.0%) were also isolated. The hexahydrophthalide distilled at 103–105° (2 mm.). Einhorn [*Ann.*, **300**, 175 (1898)] gives the boiling range as 160–165° (60 mm.). [g] Nitrophthalide, m. p. 142°, was prepared as described by Teppema [*Rec. trav. chim.*, **42**, 30 (1933)]. 5-Aminophthalide was isolated by solution of the reaction mixture in dilute hydrochloric acid, filtration of the catalyst and precipitation of the free base with ammonium hydroxide. Crystallized from ethanol the aminophthalide melted at 182°. Tasman [*ibid.*, **46**, 661 (1927)] gives the melting point as 182°.

kieselguhr to 5-aminophthalide (85% conversion), and sodium-α-hydroxy-*o*-toluate (phthalide dissolved in aqueous sodium hydroxide) yielded *o*-toluic acid (80%) on hydrogenation over nickel-on-kieselguhr.

The hydrogenation of phthalic anhydride, pthalide and various phthalide derivatives is summarized in Table I.

Experimental Part

Apparatus.—The apparatus used in this work consisted of a shaking device, high pressure steel tubes connected to recording gages, electrical pyrometers for temperature control and a source of high pressure hydrogen. The tube capacity was approximately 400 cc. In operation, the material and catalyst were charged into the tube which was then made tight with a plug and a threaded nut. A thermocouple well extended through the plug into the inner space of the tube, and a hydrogen inlet line, valve and flexible line connected to the gas manifold completed the assembly. The tube was heated and agitated mechanically, and hydrogen absorption was measured by the pressure drop in the closed system. The time of reaction given in Table I was measured from the beginning of the hydrogenation to the conclusion of the run.

Catalysts.—Nickel-on-kieselguhr catalyst was prepared from the nitrate by precipitation of the carbonate followed by hydrogen reduction according to well-known methods[3] (p. 1651). Unsupported pyrophoric nickel was prepared according to the method of Raney,[5] and copper chromite and promoted copper chromite catalysts[6] were prepared according to the standard procedures.

Isolation of Products.—Water-soluble solvents were evaporated, replaced by benzene, and the acidic components extracted with aqueous sodium carbonate. The alkaline solution was separated and acidified to give *o*-toluic acid or hexahydro-*o*-toluic acid. Phthalide was obtained by evaporation of the organic solvent and may be further purified by crystallization from alcohol or benzene. Phthalic acid, when isolated, was found in the catalyst fraction and was recovered by solution and reprecipitation from sodium carbonate solution. All of the materials isolated were characterized by means of their melting points or boiling points and by comparison with authentic specimens.

Summary

Phthalide has been obtained in excellent yields by the hydrogenation of phthalic anhydride (a) with copper chromite in benzene, (b) with Raney catalyst in ethanol and (c) with nickel-on-kieselguhr in ester or alcohol solvents. The novel use of alcohol as a solvent for this reduction has been investigated and a mechanism for the hydrogenation has been proposed. Hexahydrophthalide, 5-aminophthalide and *o*-toluic acid have been obtained in high yields by further hydrogenation of phthalide or appropriate derivatives.

WILMINGTON, DEL. RECEIVED FEBRUARY 16, 1937

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[5] Raney, U. S. Patent 1,628,190; *C. A.*, **21**, 2116 (1927).

[6] Lazier, British Patent 301,806, June 12, 1926; *C. A.*, **23**, 4306 (1929); U. S. Patent 1,746,783, Feb. 11, 1930; *C. A.*, **24**, 1649 (1930); U. S. Patent 1,964,000, June 26, 1934; Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931); Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary Systems $KClO_3$–KBr–H_2O, $KClO_3$–KI–H_2O and KIO_3–KI–H_2O at 25°

BY JOHN E. RICCI

The solubility isotherms reported in this paper were studied during the course of more extensive investigations; while no complex formation, in the form either of double compounds or of solid solutions, was found in all three systems, the results are nevertheless presented as solubility determinations which may have some interest and value. In connection with the system KIO_3–KI–H_2O, it may be mentioned that although a double compound or complex of some sort of these two salts might have been expected on the basis of the compounds known to form between sodium iodate and sodium iodide,[1] the results show no tendency at all toward compound formation between the potassium salts at 25°.

The experimental procedure was that usually employed for similar measurements. Definite mixtures of the components were stirred in a bath thermostatically controlled at 25 to ±0.02°, sufficient time (at least two days) being allowed for the attainment of equilibrium. The method of analysis of the saturated solution varied for the different systems, as follows: for the first system, the potassium bromide was determined by titration with standard silver nitrate solution, using Mohr's method; the total solid was determined by evaporation at 100° followed by 250°; and the potassium chlorate was then calculated by difference. In the second system, the potassium iodide was likewise titrated argentometrically, by Fajans' method, using eosin as the

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[1] Ricci, THIS JOURNAL, **56**, 295 (1934).

adsorption indicator, and titrating actually to the clear-point; the potassium chlorate was then calculated similarly by means of the total solid determination. In the third system, the titration of the iodide was avoided because of the insolubility of silver iodate; the potassium iodate was consequently determined directly by adding excess potassium iodide, acidifying, and titrating the liberated iodine with standard sodium thiosulfate; the determination of total solid then allowed the calculation of the original potassium iodide by difference.

The solid phases, already known in every case, were identified and verified by algebraic extrapolation of the tie-lines on the ternary diagrams, the average deviation of these extrapolations for all three systems being 0.26% from the composition of the pure solid phase. The densities reported were calculated from the weight delivered by a volumetric pipet calibrated for delivery.

The experimental results for the three systems are presented in Tables I, II and III. Figure 1 shows the isotherm for the system $KClO_3$–KBr–H_2O; the isotherms for the other two systems are very similar to this and need not be added here. The data and the plotted results show clearly that the only solid phases in the systems at this temperature are the anhydrous salts themselves, and that there is no evidence of any complex formation in the various pairs of salts.

TABLE I

SYSTEM $KClO_3$–KBr–H_2O AT 25°

Original complex, wt. %		Satd. solution, wt. %		Density	Solid phase
$KClO_3$	KBr	$KClO_3$	KBr		
...	0.00	7.905	0.00	1.047	$KClO_3$
20.55	7.73	4.59	9.30	1.100	$KClO_3$
19.60	14.07	3.21	16.99	1.160	$KClO_3$
19.06	20.00	2.41	24.20	1.216	$KClO_3$
18.98	26.09	1.87	31.66	1.292	$KClO_3$
18.99	32.38	1.42	39.47	1.376	$KClO_3$
18.98	33.47	1.43	40.00	1.385	$KClO_3$ + KBr
7.50	45.50	1.42	40.01	1.386	$KClO_3$ + KBr
1.39	50.95	1.37	40.06	1.387	$KClO_3$ + KBr
Average	(of 5)	1.42	40.01	1.385	$KClO_3$ + KBr
0.00	...	0.00	40.63	1.380	KBr

TABLE II

SYSTEM $KClO_3$–KI–H_2O AT 25°

Original complex, wt. %		Satd. solution, wt. %		Density	Solid phase
$KClO_3$	KI	$KClO_3$	KI		
...	0.00	7.905	0.00	1.047	$KClO_3$
23.15	7.52	5.04	9.33	1.103	$KClO_3$
22.03	15.09	3.35	18.74	1.178	$KClO_3$
21.49	23.06	2.30	28.72	1.275	$KClO_3$
20.97	31.52	1.60	39.26	1.400	$KClO_3$
20.68	40.06	1.10	49.94	1.555	$KClO_3$
20.01	46.98	0.82	58.34	1.702	$KClO_3$
19.98	48.22	.81	59.27	1.724	$KClO_3$ + KI
12.01	57.93	.84	59.30	1.723	$KClO_3$ + KI
2.99	66.06	.84	59.26	1.725	$KClO_3$ + KI
Average	(of 3)	.83	59.28	1.724	$KClO_3$ + KI
0.59	67.99	.67	59.36	1.724	KI
.00	...	.00	59.76	1.718	KI

TABLE III

SYSTEM KIO_3–KI–H_2O AT 25°[a]

Original complex, wt. %		Satd. solution, wt. %		Density	Solid phase
KIO_3	KI	KIO_3	KI		
...	0.00	8.449	0.00	1.071	KIO_3
22.14	2.03	7.15	2.40	1.053	KIO_3
19.87	10.11	4.33	12.04		KIO_3
18.03	19.00	3.27	22.38	1.227	KIO_3
16.99	35.01	2.54	41.10	1.451	KIO_3
16.96	48.54	2.35	57.02	1.722	KIO_3
16.96	50.06	2.36	58.54	1.749	KIO_3 + KI
8.73	58.98	2.36	58.54	1.754	KIO_3 + KI
2.19	69.14	2.35	58.47	1.749	KIO_3 + KI
Average	(of 3)	2.35	58.51	1.751	KIO_3 + KI
1.92	64.84	2.25	58.62		KI
0.81	69.91	1.10	59.14	1.731	KI
.00	...	0.00	59.76	1.718	KI

[a] Some of the determinations for this isotherm were made by Dr. John H. Wills, formerly of this department.

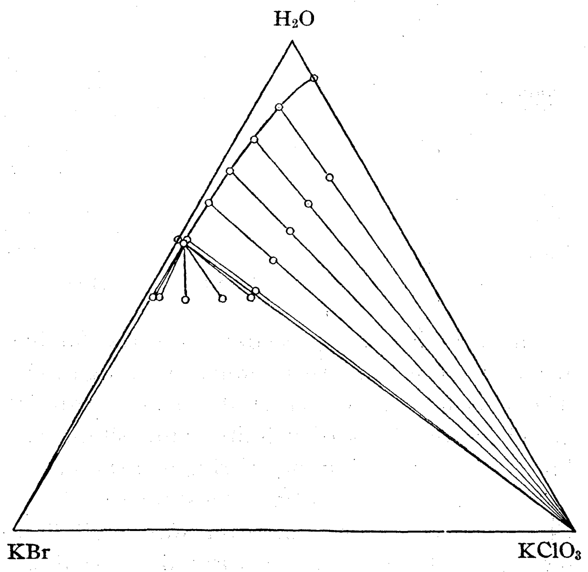

Fig. 1.—25° Isotherm: $KClO_3$–KBr–H_2O.

Summary

Solubility measurements are given for the ternary systems $KClO_3$–KBr–H_2O, $KClO_3$–KI–H_2O and KIO_3–KI–H_2O at 25°. These salt pairs are found to form neither double compounds nor solid solutions at this temperature, the only solid phases being the respective anhydrous salts.

NEW YORK, N. Y.

RECEIVED MARCH 9, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary Systems $NaNO_3$–NaBr–H_2O and $NaNO_3$–NaI–H_2O at 25°

BY JOHN E. RICCI, JOSEPH BUDISH AND NICHOLAS BORODULIA[1]

As part of the systematic phase rule investigation of ternary systems involving the alkali nitrates and halides, and for the purpose of obtaining solubility data, the ternary systems $NaNO_3$–NaBr–H_2O and $NaNO_3$–NaI–H_2O were studied at 25°. The results have shown the systems to be of the simple type at this temperature, with no complex formation, the only solid phases being the pure salts themselves, anhydrous or hydrated.

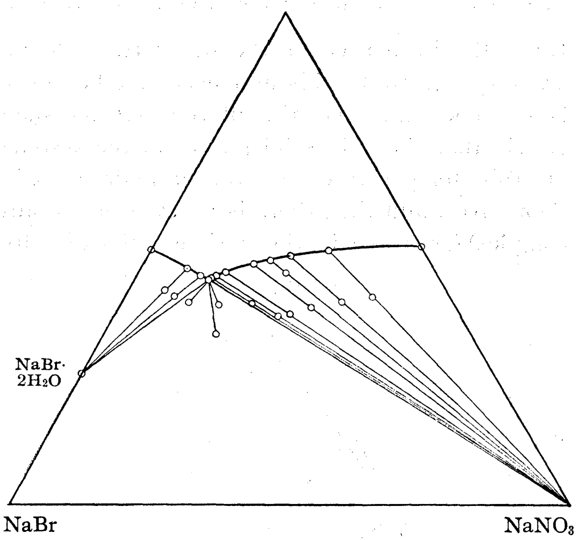

Fig. 1.—25° Isotherm: $NaNO_3$–NaBr–H_2O.

The experimental procedure was the familiar technique used in other similar investigations.[2] The salts used were recrystallized C. P. material. Weighed complexes of definite composition were brought to equilibrium by stirring in a thermostat at 25°, with the temperature constant to ±0.02°; the time allowed for equilibrium was at least two days in each case. The saturated solution was analyzed for bromide or iodide by titration with standard silver nitrate solution by means of Fajans' method, using fluorescein as the adsorption indicator, in the presence of some dextrin; this determination, combined with a determination of the total solids by proper evaporation, allowed the calculation of the sodium nitrate concentration by difference. Since no new solid phases were encountered, the phases of known composition were identified in every case by the algebraic extrapolation of the tie-lines joining the composition of the saturated solution and that of the original complex;[3] the error of these extrapolations then checks the accuracy of the analysis and the attainment of equilibrium. The average error, of extrapolation, in the $NaNO_3$–NaBr–H_2O system was 0.50%; in the $NaNO_3$–NaI–H_2O system, 0.38%.

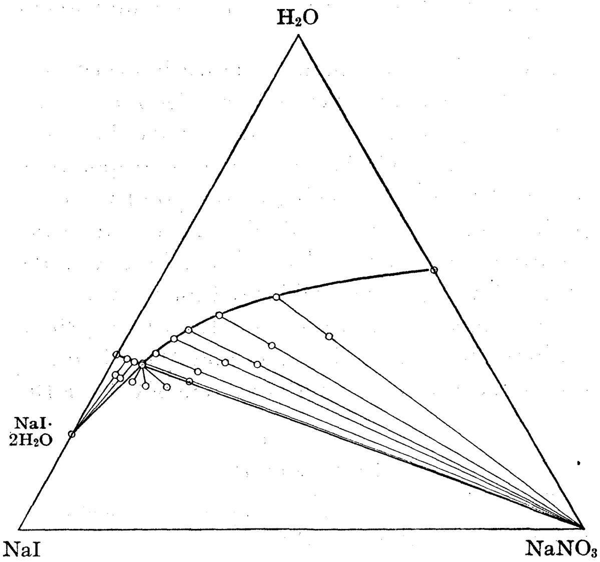

Fig. 2.—25° Isotherm: $NaNO_3$–NaI–H_2O.

TABLE I

SYSTEM $NaNO_3$–NaBr–H_2O AT 25°

Original complex, wt. %		Satd. solution, wt. %		Solid phase
$NaNO_3$	NaBr	$NaNO_3$	NaBr	
...	0.00	47.87	0.00	$NaNO_3$
43.97	13.98	31.67	17.02	$NaNO_3$
38.85	20.01	25.14	24.63	$NaNO_3$
33.96	26.00	19.80	31.54	$NaNO_3$
31.13	30.09	15.72	37.11	$NaNO_3$
28.96	33.02	14.42	39.74	$NaNO_3$
22.93	36.12	13.80	40.54	$NaNO_3$
17.68	42.10	13.64	41.03	$NaNO_3$ + NaBr·$2H_2O$
19.91	45.67	13.56	41.10	$NaNO_3$ + NaBr·$2H_2O$
11.98	46.97	13.67	41.02	$NaNO_3$ + NaBr·$2H_2O$
Average	(of 3)	13.62	41.05	$NaNO_3$ + NaBr·$2H_2O$
9.02	48.95	11.36	42.26	NaBr·$2H_2O$
6.54	50.43	8.41	44.08	NaBr·$2H_2O$
0.00	...	0.00	48.41	NaBr·$2H_2O$

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[1] Taken from work presented by Joseph Budish and Nicholas Borodulia for the Bachelor's Degree at New York University.

[2] Ricci, THIS JOURNAL, **56**, 290 (1934).

[3] Hill and Ricci, *ibid.*, **53**, 4305 (1931).

TABLE II

SYSTEM $NaNO_3$–NaI–H_2O AT 25°

Original complex, wt. %		Satd. solution, wt. %		Solid phase
$NaNO_3$	NaI	$NaNO_3$	NaI	
...	0.00	47.87	0.00	$NaNO_3$
35.90	25.27	22.57	30.49	$NaNO_3$
26.84	36.37	14.38	42.48	$NaNO_3$
26.07	40.95	10.64	49.22	$NaNO_3$
20.07	46.19	8.73	52.70	$NaNO_3$
16.01	52.02	6.77	57.64	$NaNO_3$
15.61	54.45	5.63	60.88	$NaNO_3$
9.96	60.88	5.47	61.11	$NaNO_3 + NaI \cdot 2H_2O$
8.02	62.92	5.48	61.13	$NaNO_3 + NaI \cdot 2H_2O$
5.43	64.73	5.50	61.14	$NaNO_3 + NaI \cdot 2H_2O$
Average (of 3)		5.48	61.13	$NaNO_3 + NaI \cdot 2H_2O$
2.97	66.35	3.93	62.06	$NaI \cdot 2H_2O$
2.05	67.08	2.57	63.12	$NaI \cdot 2H_2O$
0.00	...	0.00	64.71	$NaI \cdot 2H_2O$

The experimental results are presented in Tables I and II, and are shown graphically also in Figs. 1 and 2, which are self-explanatory. The solubility isotherms are seen to be of the simple two-branched type, with no evidence of any complex formation. The compositions of the isothermally invariant solutions for the two systems, are, respectively, as follows: for saturation with respect to both $NaNO_3$ and $NaBr \cdot 2H_2O$, 13.62% $NaNO_3$, 41.05% NaBr, 45.33% H_2O; for saturation with respect to $NaNO_3$ and $NaI \cdot 2H_2O$ simultaneously, 5.48% $NaNO_3$, 61.13% NaI and 33.39% H_2O. These values are in each case the averages of at least three determinations.

Summary

Solubility measurements are given for the two ternary systems $NaNO_3$–NaBr–H_2O and $NaNO_3$–NaI–H_2O at 25°; no complex formation is found, the solid phases being $NaNO_3$ and, respectively, $NaBr \cdot 2H_2O$ and $NaI \cdot 2H_2O$.

NEW YORK, N. Y. RECEIVED MARCH 15, 1937

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Abundance Ratio of the Isotopes of Potassium in Animal Tissues

BY A. KEITH BREWER

The utilization of the mass spectrograph in determining the isotope abundance ratio and the atomic weight of potassium in minerals, plants and ocean water has been discussed in recent publications.[1–3] The results indicate that the isotope ratio is not necessarily constant in nature, but in specific instances may deviate appreciably from the normal. In the present paper this investigation has been extended to a study of the potassium isotope ratio in various animal tissues.

Experimental Technique

The apparatus was essentially the same as that described previously,[1] although several improvements were incorporated. The position of the filament slit was made adjustable by means of a screw operated through a sylphon tube; this permitted a better focusing of the maximum ion beam on the filament slit. The evacuation channel was extended completely along the bottom and both sides of the pole pieces; the channel not only facilitated evacuation but served as a trap to prevent ions not in focus from being reflected into the collector slit. The entire spectrograph was heavily chromium plated and the pole pieces highly burnished; it was found that when the iron pole pieces were exposed a deposit of rust collected on the surface which, because of its poor conductivity, became charged and in consequence distorted the resolved ion beam.

The samples of tissue to be tested were washed in distilled water and then ashed in a platinum crucible. The ion source used was a small platinum disk of the type described previously. The platinum was impregnated with potassium by placing a piece of ash about the size of a pin head on the disk and moistening with distilled water. The entire filament assembly was placed in a separate evacuation system and the filament heated to just redness for about thirty minutes; during the heating process an appreciable quantity of alkali dissolves in the platinum. After heating the disk was scraped free of all visible deposit; in cases where the ash fused on heating it was necessary to remove the disk from the filament to free it from ash. The disk was then smoothed by lightly tapping between plates and rewelded in position.

Results

The abundance ratios for the two principal isotopes of potassium found in various animal sources are presented in Table I.

In the abundance ratio column limits are expressed for the apparent uncertainty for each sample. The ratios given are the averages of determinations made on several samples while the uncertainty factor represents the limits to

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(1) A. Keith Brewer, THIS JOURNAL, **58**, 365 (1936).

(2) A. Keith Brewer, *ibid.*, **58**, 370 (1936).

(3) A. Keith Brewer, *J. Chem. Phys.*, **4**, 350 (1936).

which the various readings deviated from the average. The atomic weights given are computed by assuming 1.00027 for the conversion factor from the physical to the chemical scale, and −7.0 for the packing fraction.

Discussion of the Method

The advantages of the mass spectrographic method in studying comparative atomic weights are: (1) the sensitivity is high, (2) no chemical purifications are necessary, (3) small quantities of material are required; the amount of potassium actually involved probably does not exceed 10^{-8} to 10^{-9} g. while the presence of far smaller quantities can be detected.

The possibility of error in mass spectrographic measurements may enter from two types of sources, general and functional. The general errors involve uncertainties in the isotope effect at the source, in the conversion factor from the physical to the chemical scale, and the packing fraction. None of these errors affects the relative values of the abundance ratios or the atomic weights.

Functional errors enter from an improperly operating apparatus and are not likely to affect all observations similarly. These errors have their source in some factor which gives rise to (1) a resolution of the primary ion beam between the source and the filament slit, (2) a general background which makes it difficult to measure the exact peak height, or (3) a broadening or scattering of the resolved ion beam. It is necessary to test for the presence of each of these factors in every sample to obtain comparable results. Ordinarily these difficulties are overcome by washing the filament slit free of any deposit, and by scraping all adhering ash from the disk source.

An accurate determination of the abundance ratio from measurements of the resolved ion currents necessitates that all the ions of the isotope in question which pass through the filament slit reach the collector. This was made possible in the present set-up by using filament and collector slits 0.22 mm. and 0.77 mm. in width, respectively; the width of the collector slit is thus appreciably greater than that of the resolved ion beam provided no scattering of the beam occurs. Under proper operating conditions the flat top of the K^{39} peak was one-fifth the width of the separation between the center of the K^{39} and K^{41} peaks. Since scattering tended to broaden the beam, it was discernible by a sharpening of the resolved peaks. It was found in practice that particles of ash which had not been removed from the disk and irregularities in the disk itself were responsible for most of the scattering.

Considering the various sources of error and nonuniformity in the results that are involved, it seems probable that the sixth significant figure in the comparative atomic weight calculations is accurate to within ±1 to ±5 depending on the sample. No such accuracy, however, can be claimed for the absolute value of the atomic weight. In this respect it should be pointed out that an abundance ratio of 14.20 gives 39.094 for the atomic weight using the most probable values for the packing fraction and the conversion factor, but since either of these quantities may be in error by as much as one part in 10,000, the atomic weight as computed may be inaccurate by as much as ±4 in the fifth significant figure. The calculated values in Table I, are included for comparative purposes only.

Significance

There are very few references in the literature relative to an isotope effect for potassium in the animal organisms. Potassium, nevertheless, is without doubt the most interesting of all the elements in this connection, since it is the only element necessary to the vital process that is radioactive, one of its isotopes emitting two hard β rays. Ernst[4] making use of this radioactivity reports that potassium from human and animal sources is more radioactive than normal. A. and M. Lasnitzki[5] observe some differentiation between mineral and biological potassium in the feeding of mice. A general review of the effect of natural processes on the isotope ratio has been given by Vernadsky.[6]

A survey of the data presented in Table I shows that the isotope abundance ratio for potassium in most animal tissues is close to 14.20; this is the same as that for sea water and the majority of plants and minerals. In only a few instances are any marked deviations from the normal to be found. The heart muscles and especially the lining of the right auricle as well as the membranes supporting the valves are inclined to be low in K^{41}. The heart was tested in parti-

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(4) E. Ernst., *Naturwissenschaften*, **22**, 479 (1934).

(5) A. and M. Lasnitzki, *Nature*, **138**, 800 (1936).

(6) W. I. Vernadsky, *Compt. rend. acad. sci. U. R. S. S.*, **3**, 129 (1936).

TABLE I

ABUNDANCE RATIO AND COMPUTED ATOMIC WEIGHT OF POTASSIUM IN VARIOUS ANIMAL TISSUES

Source of sample		Part	K^{39}/K^{41}	% K^{41}	Calcd. at. wt.
Horse	30 years	Marrow	13.90 ± 0.03	6.71	39.0967
Horse	26 years	Marrow	13.92 ± .04	6.70	39.0965
Beef	Bull (old)	Marrow	13.80 ± .02	6.76	39.0975
Beef	Bull (old)	Marrow oil	13.90 ± .05	6.71	39.0967
Beef	Bull (old)	Marrow hard	13.68 ± .03	6.81	39.0986
Beef	Veal	Marrow	13.70 ± .03	6.80	39.0985
Beef	Mature	Marrow	13.83 ± .02	6.74	39.0973
Beef	Mature	Bone	14.03 ± .02	6.65	39.0955
Beef	Mature	Red meat	14.21 ± .01	6.58	39.0939
Beef	Mature	Thyroid	14.21 ± .02	6.58	39.0939
Beef	Mature A	Kidney	14.22 ± .03	6.57	39.0938
Beef	Mature B	Kidney (Leached)	14.21 ± .03	6.58	39.0939
Beef	Mature	Suet	14.21 ± .01	6.58	39.0939
Beef	Mature	Liver	14.20 ± .03	6.58	39.0940
Beef	Mature	Liver extract	14.23 ± .03	6.57	39.0938
Pork		Liver	14.21 ± .03	6.58	39.0939
Pork		Pancreas	14.24 ± .02	6.56	39.0937
Pork		Lung	14.16 ± .01	6.60	39.0934
Pork		Adrenal	14.21 ± .01	6.58	39.0939
Pork		Kidney	14.19 ± .02	6.58	39.0941
Pork		Stomach	14.22 ± .01	6.57	39.0938
Pork		Pituitary	14.17 ± .02	6.59	39.0943
Pork		Ventricle muscle	14.20 ± .01	6.58	39.0940
Pork		Auricle muscle	14.24 ± .02	6.56	39.0937
Pork		Auricle membrane	14.28 ± .03	6.55	39.0933
Pork		Blood	14.23 ± .03	6.57	39.0938
Pork		Intestines	14.25 ± .02	6.56	39.0935
Mutton		Cartilage	14.13 ± .02	6.62	39.0946
Mutton		Suet	14.20 ± .02	6.58	39.0940
Oyster			14.19 ± .02	6.58	39.0941

cular since it has long been known that potassium in the blood is a factor in regulating heart beat, and since Zwaardemaker[7] and Loeb[8] have raised the question of the effect of the radioactive potassium isotope on beat stimulation. The results indicate that the lining of the auricle may contain less than the normal amount of the radioactive isotope. Some uncertainty still remains regarding which potassium isotopes are responsible for the radioactivity although the abundant isotope K^{39} is known to be non-radioactive. Recently Smyth and Hemmendinger[9] have shown that the exceedingly rare isotope K^{40} is responsible for part and possibly all of the radioactivity. Any process, however, that will concentrate K^{41} will doubtless concentrate K^{40}; in consequence an abundance ratio below 14.20 should represent a radioactivity above normal. The facts that this radioactivity is feeble and that the deviations in the abundance ratio recorded in Table I are small make it seem very doubtful whether the potassium from various tissues is distinguishable by radioactive measurements. The relative abundance of K^{40} has been measured by A. O. Nier[10] and by the writer[11] but measurements of the K^{39}/K^{40} ratio involve too much uncertainty for a comparison of various sources.

The most conspicuous concentration of K^{41} was observed in bone marrow. The data, while insufficient, indicate a possible dependence of the abundance ratio on the age of the animal; in all the cases examined the ratio was higher for young than for old animals. It should be mentioned that bone marrow was investigated in some detail, since Hoffmann[12] had shown that the potassium content appears to be associated with embryonic cell development, diminishing markedly at the conclusion of growth activity, and increasing again on the development of carcinoma. Unfortunately, it was not possible to make abundance ratio tests on any cancerous animals.

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(7) H. Zwaardemaker, *Geneesk Blader*, **20**, 253 (1918); *J. Physiol.*, **55**, 33 (1921).

(8) J. Loeb, *J. Gen. Physiol.*, **3**, 229 (1920).

(9) W. R. Smyth and A. Hemmendinger, *Phys. Rev.*, **51**, 146 (1937).

(10) A. O. Nier, *ibid.*, **50**, 1041 (1936).

(11) A. Keith Brewer, *ibid.*, **48**, 640 (1935).

(12) T. Hoffmann, *Biochem. Z.*, **243**, 145 (1931).

In conclusion it should be mentioned that while the deviations which have been reported for animal and plant tissues are small, they are nevertheless appreciable. Deviations of this magnitude are exceedingly difficult to produce in the laboratory; the writer has tried several times himself and has examined many samples prepared by eminent scientists but in no instance has a definite isotope shift been observed. While it is possible to conjecture concerning the mechanism of the isotope effect in nature, the data are still too meager to permit any definite conclusion to be drawn.

The writer is indebted to Mr. N. G. Barbella, of the Bureau of Animal Industry for furnishing many of the samples tested.

Summary

The abundance ratio of the two principal isotopes of potassium present in animal tissues have been measured with a mass spectrograph. The K^{39}/K^{41} ratio for most organs is close to 14.20, which is the same as that previously obtained for most plants and minerals and for ocean water. A few tissues, such as the lining of the auricle and the lining of the small intestine, appear to possess an abnormally high concentration of K^{39}, while bone marrow is high in K^{41}. The results with bone marrow are significant in that they indicate a possible relationship between the abundance ratio and the age of the animal, and hence with the development of embryonic cells within the organism.

The atomic weight of potassium has been calculated using the most probable values for the packing fraction and the conversion factor; the value thus obtained for most tissues is 39.094. Since all deviations from this normal value are small, it does not seem probable that the potassium in animal tissue could be distinguished from mineral potassium by radioactive measurements as has been suggested by some investigators.

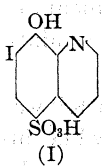
WASHINGTON, D. C. RECEIVED MARCH 13, 1937

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

A Study of 7-Iodo-8-hydroxyquinoline-5-sulfonic Acid as a Reagent for the Colorimetric Determination of Ferric Iron[1]

BY JOHN H. YOE AND ROBERT T. HALL[2]

In 1932 Yoe[3] reported a method for the colorimetric determination of iron by means of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (I).[4] It was found that this compound reacts instantaneously with ferric ions yielding green colored solutions, the color intensity varying with the iron concentration. The reaction is very sensitive and may be used to determine ferric iron in the presence of ferrous, since the latter produces no color with the reagent. Also, the color does not fade on standing, which is an advantage over the thiocyanate method as frequently carried out in acid solution.



(I)

In view of the advantages offered by this method, namely, the stability of the colored compound, the high sensitivity of the reaction, and its ability to distinguish between ferric and ferrous ions, it seemed desirable to investigate it in detail. In fact, the reagent appears to be specific for ferric ions, since no other ion has been found to yield a color reaction with Ferron.[3]

The following studies have been made on the reagent and its reaction with ferric ions: solubility in various solvents; nature of the color reaction; physical and chemical properties of Ferron; influence of various ions; sensitivity; Lambert–Beer law; effect of hydrogen-ion concentration; aging effect and the effect of temperature.

Reagents and Solutions.—The general technique and method of investigation has been described in a previous paper by Yoe and Wirsing.[5] 7-Iodo-8-hydroxyquinoline-5-sulfonic acid (Ferron) was first prepared by Claus.[6] The compound used in this investigation was a very pure product obtained from G. D. Searle and Co., Chicago, Ill. A saturated aqueous solution (approximately 0.2%) of Ferron makes a satisfactory reagent solution. For convenience in obtaining various molecular ratios between the Ferron and ferric iron, several other Ferron solutions of known concentration were prepared.

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(1) Original manuscript received April 11, 1936.

(2) Present address, Swann and Company, Birmingham, Ala.

(3) Yoe, THIS JOURNAL, **54**, 4139 (1932).

(4) On account of the lengthy name of this compound we are proposing that it be called "Ferron."

(5) Yoe and Wirsing, THIS JOURNAL, **54**, 1866 (1932).

(6) Claus, *Friedl.*, **3**, 964 (1892).

The standard iron solution was prepared from ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, reagent quality, 0.7020 g. of the salt being weighed out and dissolved in about 100 ml. of distilled water. Five milliliters of concentrated sulfuric acid (iron-free) was then added to the solution to prevent hydrolysis. Five to ten milliliters of saturated bromine water was added and the solution boiled until the iron was oxidized and the excess bromine expelled. The solution was then cooled and diluted to a liter in a volumetric flask. Its iron content was checked volumetrically by reducing (with the Jones reductor) the ferric sulfate solution and titrating immediately with a potassium permanganate solution which had been standardized against sodium oxalate obtained from the National Bureau of Standards. The average of three determinations in close agreement gave the iron concentration as 0.1005 g. per liter. This solution was used as a stock solution from which more dilute ones were conveniently prepared as needed.

Solutions of the salts used in studying the effects of various ions were prepared so that 1 ml. would contain 2 mg. of the desired ion, assuming complete dissociation. Chlorides, nitrates and sulfates were employed and, when necessary, they were recrystallized from conductivity water until iron-free.

The buffer solutions were prepared from various standard solutions according to the directions of Clark.[7]

Apparatus.—For the solubility measurements, a large thermostat equipped with an immersed, rotating wheel was used. Its temperature was maintained constant at 25 to ±0.1°. Standard types of apparatus and methods were employed in making the *p*H determinations. In making color comparisons, a daylight lamp and Duboscq colorimeter (Bausch and Lomb) were always used in fixed positions in a dark room. Also a set of twelve carefully matched 50-ml. Nessler tubes (210-mm.) was used. These were placed in a shielded Nessler tube rack.

All weights, pipets and volumetric flasks were calibrated. The reagents were measured out with pipets which were labelled so that a given pipet was always used for one solution only.

Composition of Ferron.—An ultimate analysis was made of the 7-iodo-8-hydroxyquinoline-5-sulfonic acid, using standard methods. The results of the analysis are summarized in Table I.

Table I

Constituent	Found	Calcd.
Carbon	30.68	30.76
Hydrogen	1.62	1.72
Oxygen[a]	18.43	18.27
Nitrogen	4.03	3.99
Sulfur[b]	9.04	9.11
Iodine[b]	36.06	36.15

[a] Obtained by difference.

[b] Average of three analyses.

Experimental

Solubility of Ferron.—The solubility of 7-iodo-8-hydroxyquinoline-5-sulfonic acid in several solvents and mixtures of solvents was determined at 25°. Into clean 100-ml. glass-stoppered Pyrex bottles was introduced 50 ml. of the solvent and sufficient of the Ferron so that after thorough agitation a few tenths of a gram of the solid settled out. The bottles were tightly stoppered, firmly attached to the thermostat wheel, rotated for twenty hours and then allowed to stand for sixteen hours. Without removing the bottles from the thermostat, 25 ml. of the clear supernatant liquid was withdrawn and introduced into dried weighed crucibles. The solutions were evaporated to dryness in vacuum desiccators and the crucibles plus their contents then weighed. The data are recorded in Table II.

Table II

Solubility of Ferron at 25 ±0.1°

Solvent	Solubility, g./100 ml. soln.
Acetone	0.0080
Glacial acetic acid	.0192
Alcohol (absolute)	.0304
Water	.2220
Water–alcohol (1:1 by vol.)	.3500
Water–alcohol (3:2 by vol.)	.5696
Water–acetone (1:1 by vol.)	.7200

It is interesting to note that the mixtures have a greater solvent action than the individual solvents. The presence of the sulfonic acid group in the compound probably causes it to have a greater solubility in water than in an organic solvent. If the compound did not contain the sulfonic acid group, it would be expected to be more soluble in an organic solvent than in water. Therefore it might be predicted that the maximum solubility would be attained in a mixture of water and an organic solvent. Such was found to be the case.

Physical and Chemical Properties of Ferron.—7-Iodo-8-hydroxyquinoline-5-sulfonic acid is a bright yellow crystalline solid. On slow heating it changes from a yellow color to a dark brown at 225°, and at 250° turns completely black, decomposition occurring without melting. On rapid heating it melts sharply at 285°, at the same time undergoing decomposition as is indicated by an evolution of iodine vapor. Boiling its aqueous solution causes a slow decomposition with the evolution of a trace of iodine, easily detected by its odor. Also, the aqueous solution on standing for several weeks takes on a slightly darker shade of yellow due to the presence of a little iodine liberated by the compound. However, such solutions are quite satisfactory for colorimetric work.

Nature of the Reaction.—The exact reaction that takes place between 7-iodo-8-hydroxy-

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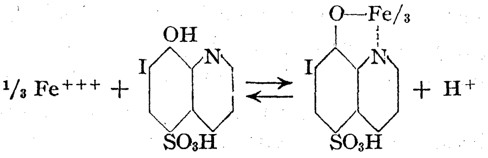
[7] Clark, "The Determination of Hydrogen Ions," 3d ed., Williams and Wilkins Co., Baltimore, Md., 1928.

quinoline-5-sulfonic acid and ferric ions is not known with certainty. In the first part of our work aqueous solutions of the reagent were prepared in such concentrations that when added to known amounts of ferric iron, there existed a definite molecular ratio between the iron and the reagent. By changing these molecular ratios both the color and the intensity could be varied. It was reasoned that if the molecular ratio in which the ferric ions and the reagent combine to give the optimum color formation could be determined, this might give some information as to the probable reaction. With this in view a number of solutions were prepared for observation in Nessler tubes and in the colorimeter. The molecular ratios of the reagent to ferric iron in these solutions were varied widely and covered the range from 0.5 mole of reagent : 1 mole of ferric iron to 6 moles of reagent : 1 mole of ferric iron. The reagent solutions were prepared in varying concentrations so that the same volume of reagent was added to the iron solution in each case, although different molecular ratios existed after final dilution. The amount of iron was constant throughout.

The color studies indicated that 1 mole of ferric iron requires at least 1 mole of reagent but not more than 3 moles. Color studies were made on the three molecular ratios, 1:1, 2:1 and 3:1. The evidence in all cases pointed to a 3:1 molecular reaction between Ferron and ferric iron, *i. e.*, one equivalent weight of ferric iron requires one mole of the reagent. The reaction may be expressed by



This reaction is in accord with the work of Berg[8] on the complex metal salts of *o*-hydroxyquinoline. Berg postulated that the hydrogen of the hydroxyl group, due to the position of this group relative to the quinoline nucleus, had its activity enhanced and that the compound reacting with metals formed an inner complex salt. However, it should be noted that our conclusions concerning this reaction are based purely on color formation and of course cannot be considered as a rigid proof. Attempts to obtain the colored compound in a crystalline form were unsuccessful. Slow evaporation at room temperature always yielded a dark green amorphous mass. In any case, in the preparation of a standard series, at least enough reagent should be added to use up all the iron on the basis of a 3:1 reaction, *i. e.*, 3 moles of Ferron to 1 gram-atom of iron.

Influence of Various Ions.—In the preliminary investigation Yoe[3] found that ferric ions are the only ions which give a color reaction with 7-iodo-8-hydroxyquinoline-5-sulfonic acid. He also pointed out that salts which hydrolyze easily, or yield colored ions, interfere with the color reaction. Therefore a quantitative study of the effect of various ions likely to be encountered in analyses was made. Aqueous solutions containing known amounts of ferric iron plus various other ions were prepared. The amount of iron in these solutions was then determined by comparison with standards. The procedure was as follows: measured quantities of the metallic salts were placed in Nessler tubes and to each tube was added a known amount of ferric iron. The acidity was adjusted to a *p*H of about 2.5 by adding hydrochloric acid–potassium acid phthalate buffer solution. The reagent was then added, the solutions diluted to the mark, thoroughly mixed and compared with a series of standards. The results are shown in Tables III and IV.

Table III

Concentration of Ions in Parts per Million

Soln.	Metal ions	Metal ions	Fe^{+++} Present	Fe^{+++} Found
1	Al^{+++} 7.0		1.0	No match
2	Al^{+++} 2.5		0.5	0.5
3	Al^{+++} 5.0		.5	No match
4	Al^{+++} 5.0		1.0	1.0
5	Al^{+++} 10.0		1.0	No match
6	Al^{+++} 30.0		6.0	6.0
7	Co^{++} 1.6		0.5	No match
8	Co^{++} 2.0		1.0	1.0
9	Co^{++} 0.8	Ni^{++} 0.8	0.5	0.5
10	Fe^{++} 2.0		2.0	2.0
11	Fe^{++} 1.0		0.4	0.4
12	Co^{++} 4.0	Ni^{++} 4.0	4.0	4.0
13	Co^{++} 6.0	Ni^{++} 6.0	6.0	6.0
14	Co^{++} 1.0	Ni^{++} 1.0	0.5	No match
15		Cr^{+++} 1.0	.5	0.5
16	Al^{+++} 10.0	Cr^{+++} 10.0	5.0	5.4
17		Cr^{+++} 10.0	5.0	5.2
18		Cr^{+++} 1.4	0.5	0.5
19		Cr^{+++} 20.0	.5	No match
20		Cr^{+++} 3.0	5.0	5.0
21	Ti^{++++} 0.2		0.5	0.5
22	.3		.5	No match
23	20.0		5.0	No match

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[8] Berg, *J. prakt. Chem.*, **115**, 178 (1927); *Z. anal. Chem.*, **70**, 341 (1927).

Table IV

Concentration of Ions in Parts per Million

Soln.	Metal ions	Fe^{+++} Present	Fe^{+++} Found
1	Sn^{++} 0.1	0.4	No match
2	Sn^{++} .1	1.0	No match
3	Sn^{++++} .8	2.0	2.0
4	Sn^{++++} 2.0	2.0	No match
5	Sn^{++++} 1.2	0.5	0.5
6	Sn^{++++} 1.2	2.0	2.0
7	Cu^{++} 0.4	0.5	Color bleached
8	Cu^{++} .3	1.0	Color bleached
9	$Cr_2O_7^{=}$ .4	0.5	No match
10	$Cr_2O_7^{=}$ .2	2.0	No match
11	NO_2^- 1.0	2.0	No match
12	NO_2^- 0.2	0.5	No match
13	NO_2^- .2	2.0	No match

The data in Table III show that colored ions should not be present except to a limited extent. Aluminum may be present in an amount approximately five times that of ferric iron without causing marked interference. Colbalt and nickel may be present individually in proportions about twice as great as iron. Titanium should not be present in a concentration greater than a few tenths of a part per million. The chromium concentration should not exceed that of the iron. The effect of the above colored ions appears to be additive. It is of particular interest to note that ferrous iron may be present without causing the least difficulty in the determination of the ferric iron.

Table IV records the ions that cause the most difficulty. These ions must not be present in concentrations greater than a few tenths of a part per million. For precise work they should be removed totally. Cupric ions interfere when present to the extent of only 0.2 p. p. m. Salts that hydrolyze easily, such as those of tin and titanium, should be removed before an iron determination is made. It should also be pointed out that fluoride causes a partial bleaching of the color and must be absent. Relatively large amounts of phosphate may prevent the immediate formation of maximum green color intensity but on standing (five minutes to two hours) the maximum intensity develops.

Sulfate, nitrate and chloride ions do not interfere with the color reaction.

Sensitivity.—The sensitivity measurements were made according to the method described by Yoe and Wirsing.[5] The results are recorded in Table V.

In Table V column 1 gives the concentration stated as liters containing one gram-atom of iron.

Table V

V	B	Δ	S	B'	B/B'
7,977	0.3500	Too intense for observation			
15,954	.1750	0.0125	80	0.1875	0.933
21,476	.1300	.0075	133	.1375	.945
31,023	.0900	.0050	200	.0950	.947
50,950	.0548	.0037	266	.0585	.936
186,133	.0150	.0025	400	.0175	.857
310,230	.0090	.0020	500	.0110	.820
1,116,800	.0025	Barely distinguishable from blank			

In the second column B is the total milligrams of iron in 50 ml. of solution. Δ is the mg. of iron producing a perceptible difference in the color intensity of 50 ml. of solution. S is the sensitivity and is the reciprocal of the figures recorded in column 3. $B' = B + \Delta$.

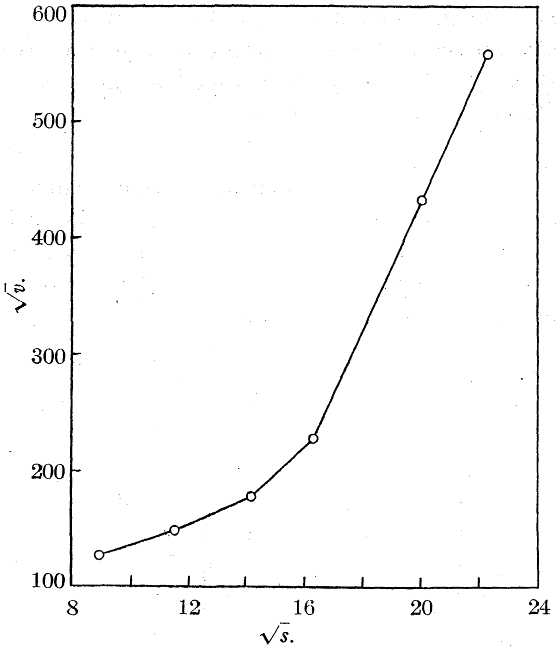

Fig. 1.

Figure 1 shows graphically how the sensitivity varies with the concentration. For convenience in plotting, the square roots of the volume and sensitivity were used. The sensitivity curve for iron is very similar to those obtained by Yoe and Hill[9] for aluminum and by Yoe and Wirsing[5] for nickel. The portion of the curve having the least slope is the range of maximum sensitivity. Except for this portion and at very dilute solutions the sensitivity is a straight line function of the concentration.

Horn[10] has suggested that the ratio B/B' is probably constant throughout colorimetry,

(9) Yoe and Hill, This Journal, **50**, 748 (1928).

(10) Horn, *Am. Chem. J.*, **35**, 253 (1906).

independent of the color examined. The data in Table VI are in agreement with this hypothesis.

TABLE VI

Ion	Method	Color	B/B' av.	Observer
Al^{+++}	"Aluminon"	Red	0.92	Yoe and Hill
Al^{+++}	Alizarin	Red	.89	Yoe and Hill
$CrO_4^{=}$	$CrO_4^{=}$	Yellow	.96	Horn
Cu^{++}	Cu^{++}	Blue	.92	Horn and Blake
Cu^{++}	$Cu(NH_3)_4^{++}$	Dark blue	.95	Horn and Blake
Ni^{++}	$K_2NiC_4O_4S_4$	Magenta	.95	Yoe and Wirsing
Fe^{+++}	$C_9H_6NOIHSO_3$	Green	.93	Yoe and Hall

Our experiments showed that the Ferron reagent will determine quantitatively as little as 0.1 mg. of iron in a liter of solution, that is, 1 part in 10 millions.

Lambert-Beer Law.—In the case of colored solutions, the absorption of light depends not only on the thickness of the layer traversed, but also on the molecular concentration in the layer. Beer (1852) therefore modified Lambert's law (1760) and expressed it as

$$I = I_0^{-kcl} \qquad (1)$$

in which k is the molecular absorption coefficient; c is the molecular concentration; I is the intensity of the light after passing through the thickness, l, of the medium and I_0 is the intensity of the incident light upon the medium.

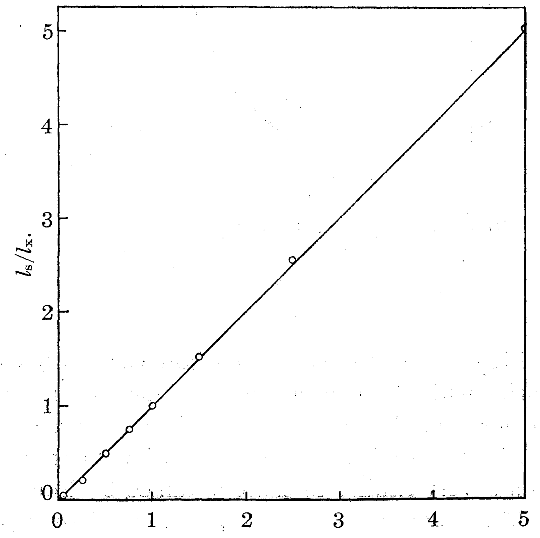

Fig. 2.

As applied to colorimetry, the Lambert-Beer law is generally expressed in the following more convenient form

$$c_x/c_s = l_s/l_x \qquad (2)$$

where c_s and c_x represent the concentrations of the standard and "unknown," respectively, and l_s and l_x are the readings of the heights of the standard and "unknown" solutions, respectively.

According to equation (2) when equal color intensity is obtained from different heights of two solutions, the concentrations are inversely proportional to the heights. In order for this relationship to hold, the color formation in the two solutions must be perfectly formed, or imperfectly formed to the same extent in both solutions. When this is not the case the difficulty must be overcome by the use of a calibration curve which can be prepared experimentally from solutions of known concentrations.

For the study of the Lambert-Beer law colored solutions of various concentrations were prepared from the stock (standard) iron solution and each solution was then matched against the standard colored solution in a B. and L. Duboscq colorimeter. The amount of Ferron added in each case was sufficient to satisfy a 3:1 molecular reaction. The pH of the solutions was kept constant at 2.6 by the use of hydrochloric acid-potassium acid phthalate buffer solution. The data are shown graphically in Fig. 2. According to the Lambert-Beer law a straight line would be obtained by plotting the ratio of heights against the inverse ratio of concentrations. An examination of Fig. 2 shows that the law is followed, within the experimental error, over the range of concentration examined.

Effect of Hydrogen-Ion Concentration.—The hydrogen-ion concentration has a pronounced influence on the reaction between ferric ions and Ferron. Yoe[3] reported that the reaction is best carried out in a solution acid to methyl orange paper, and that the color was completely destroyed by the addition of either strong acid or alkali. In this work a more extensive study of the effect of hydrogen-ion concentration was made and the optimum pH range for the color reaction was determined.

First of all, a study was made of the sensitivity of the reagent solution to hydrogen-ion concentration. It was found that below a pH of 1.2 and above a pH of 8.3 the reagent solution was completely decolorized. However, over the pH range from 2 to 3 there was only a slight change in the color intensity of the reagent solution.

Experiments with the colored iron solutions showed that once the color is formed it could exist with varying intensities over a fairly wide pH range (2 to 5 approximately). The color intensity of iron solutions of the same concentration shows no perceptible variation over a *p*H range from 2 to 3, but it was noted in all of this work that above *p*H 3.0 a very small change in hydrogen-ion concentration had a pronounced effect on the color intensity. Since in the *p*H range from 2 to 3 the color intensity is constant and reproducible, in practice, the hydrogen-ion concentration should be adjusted to a *p*H of approximately 2.5. It was found that this could be done with a precision of ±0.2 *p*H by the use of hydrochloric acid–potassium acid phthalate buffer. This buffer does not, in any respect, interfere with the color reaction.

Aging Effect.—In many colorimetric methods the color formed has the unfortunate property of fading rapidly on standing, thus making it necessary to make the color comparison at once. Moreover, the standard color solutions must be made up fresh for each determination, unless it be possible to obtain satisfactory permanent standards made from stable colored compounds. In this investigation a thorough study was made of the effect of aging on the green colored solution. Both Nessler tubes and a Bausch and Lomb Duboscq colorimeter were used in this study. It was found that a colored solution which had aged thirty-six days still matched a freshly prepared solution of the same concentration.

Effect of Temperature.—The temperatures of various colored solutions of the same iron concentration were fixed at different values, covering a range from 15 to 40° and observations were made on them in Nessler tubes. No color changes or changes in intensity could be detected. Hence, variations that occur within the range of laboratory temperatures have no effect on the color.

Optimum Experimental Conditions.—The results of the studies made on the various factors involved enabled the establishment of certain experimental conditions under which the color reaction should be carried out in order to obtain the most satisfactory results. Sufficient reagent solution should be added to react with all the ferric iron present on the basis of a 3:1 molecular ratio. However, for Nessler tube work it was found convenient to add a fixed amount of reagent over a whole range of iron concentration. For iron concentrations less than 1 p. p. m., prepare a solution free from any interfering ions, adjust the acidity to a *p*H of 2.5 by means of hydrochloric acid–potassium acid phthalate buffer and add 5 drops (0.25 ml.) of the Ferron reagent. The color develops at once. Dilute to the mark with distilled water and mix thoroughly.

For iron concentrations from 1.0 p.p.m. to 2.0 p. p. m., 1 ml. of the reagent solution is added and for concentrations above 2.0 p. p. m., add 2 ml. of reagent. Due to the great intensity of the green color formed, precise matching is impossible for concentrations greater than 4.0 p. p. m. of Fe^{+++}. In other words, with 50-ml. Nessler tubes (tall form), the range is from 0.005 to 0.2 mg. of ferric iron. Matching is much more easily made over the range from 0.0075 mg. iron per ml. to 0.05 mg. per ml.

In the analysis of unknowns it sometimes happens that a very large excess of reagent is used in preparing both the standard and the unknown. A Corning HR yellow filter No. 351 will be helpful in eliminating the effect of excess reagent.

It must be borne in mind that the use of a buffer solution alone to adjust the *p*H is governed by some practical considerations, the most important of which is that the amount of buffer solution used has a limited capacity to prevent appreciable changes in hydrogen-ion concentration. It is possible that an unknown might be so strongly acidic or basic that the buffer could not hold the *p*H within the required range. For this reason the sample solution should always be tested with an indicator paper (Congo red or methyl orange) and the *p*H approximately adjusted, if too acid or too alkaline.

Determination of Iron in Various Materials

The colorimetric method described in the preceding section has been used for the determination of iron in a large number of the National Bureau of Standards samples. The samples analyzed varied widely in their chemical nature and included such materials as bauxite, feldspar, glass sands, glasses, clays, limestones and alloys. Hence, it was possible to try out the method over a wide range of conditions.

The colorimetric part of these analyses was done by means of the standard series method using 50-ml. Nessler tubes (tall form). The sensitivity data showed that the concentration range from 1 to 2 p. p. m. of Fe^{+++} was within the range of greatest sensitivity. A difference in iron content of 5 γ could be detected. If the magnitude of the amount of iron in the sample was known, then the weight of sample to be taken for analysis could be calculated, so that the concentration of the solution finally analyzed fell within the range of maximum sensitivity. When the approximate iron content was unknown (to the analyst), a rough preliminary analysis was made to determine the correct size of sample to be taken. All samples were issued to one of us (R. T. H.) as unknowns.

In general, the procedures used in the analyses of the various samples followed closely those given in the National Bureau of Standards Certificates of Analyses. In many cases it was possible to simplify these considerably, since in this work only one constituent was sought. For convenience, the materials analyzed may be classified into three groups: glass sand and glass, rocks and alloys.

Methods of Analysis

After investigating several procedures, the following was found to be the most satisfactory for glass sand and glass.

Glass Sand and Glass.—A sample of about 0.25 g. was weighed out after the material had first been dried at 110°. The weight of sample to be taken was governed by certain considerations already pointed out. The sample was then fused to a clear melt in a platinum crucible, using sodium carbonate as a flux. The fusion, after cooling, was disintegrated and treated by the perchloric acid method[11] for the dehydration of silicic acid. The silica was filtered off, washed thoroughly with dilute hydrochloric acid and finally with water. The filtrate was received in a porcelain casserole and its acidity adjusted by the addition of concentrated ammonium hydroxide until it was just acid to Congo red paper. The solution was evaporated on the steam-bath to such volume that it could be introduced into a Nessler tube along with 10 ml. of buffer solution (pH 2.6) and 1 ml. of the Ferron reagent. This Nessler was then compared with a standard series, and a match obtained. In some cases, instead of evaporating the solution to a small volume, it was found convenient to dilute it to a known volume in a volumetric flask and then remove an aliquot for analysis. In all these analyses the pH of the standard and of the unknown was determined. In every case the pH was within the range of 2.6 ± 0.2, and usually did not vary more than 0.1 of a pH unit.

When aluminum was present in amounts relatively large in comparison with the amount of iron, as was the case in a few of the samples, it interfered to some extent with the determination. This difficulty was overcome either by adding a little aluminum salt to the standard in cases where the aluminum content was known or by separating the iron from the aluminum (by means of sodium hydroxide) in the manner given by Hillebrand and Lundell.[11] In some instances it was necessary also to remove the titanium. The iron was separated from both the aluminum and the titanium according to the National Bureau of Standards method.[12]

Rocks and Clays.—Included in this group were the following: bauxite, plastic clay, fluorspar, feldspar, dolomite and argillaceous limestone. The procedures used for these samples were for the most part based on the methods of the National Bureau of Standards. Aluminum and titanium were present throughout this whole group and in most instances it was necessary to remove these constituents in order to make a satisfactory determination of the iron. The methods used on bauxite and plastic clay were essentially the same as the one given by Lundell and Hoffman.[13] The fluorspar, feldspar, and limestones were analyzed according to standard methods and the iron determined colorimetrically by Ferron.

Alloys.—The iron content of the following alloys was determined colorimetrically by means of the Ferron reagent: sheet brass, cast bronze and zinc base die-casting alloy. The elements copper, tin and antimony were present in varying amounts in all of these materials and nickel was present in two of them. It had previously been found that all of these elements interfere with the Ferron method for iron. The separation of these elements from the relatively small amount of iron present in the samples was extremely difficult in some cases. The sheet brass and cast bronze were analyzed according to a procedure developed by Lundell and Scherrer.[14] Of the constituents in the zinc base die-casting alloy, only the copper and aluminum were present in amounts sufficient to make their elimination necessary.

The results of all analyses are summarized in Table VII.

TABLE VII

Material	B. of S. No.	Total iron as Fe_2O_3	
		B. of S. Av.	Found
Bauxite	69	5.66	5.72
Clay, plastic	98	2.05	2.00
Dolomite	88	0.084	0.092
Dolomite	88	.084	.095
Feldspar	70	.03	.037
Feldspar	70	.03	.04
Fluorspar	79	.15	.14
Glass, boron	93	.076	.077
Glass, lead barium	89	.049	.052
Glass, opal	91	.081[a]	.075
Glass, soda lime	80	.065	.062
Glass sand	81	.073[b]	.067
Limestone, argillaceous	1A	1.63	1.64
		Total iron as Fe	
Cast bronze	52	0.12	0.08
Sheet brass	37B	.21	.18
Sheet brass	37B	.21	.18
Zinc base die-casting alloy	94	.048	.037
Zinc base die-casting alloy	94	.048	.040

[a] Colorimetric method gave value of 0.070. [b] Colorimetric KCNS method gave values of 0.067 and 0.068, respectively, by two analysts.

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(11) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929.

(12) National Bureau of Standards Certificate of Analysis for Standard Sample No. 69.

(13) Lundell and Hoffman, *Bur. Standards J. Research*, **1**, 91 (1928).

(14) Lundell and Scherer, *Ind. Eng. Chem.*, **14**, 426 (1922).

An examination of the table shows that with one or two exceptions the results are in good agreement with those reported by the National Bureau of Standards. The low percentages obtained on the alloys undoubtedly were due to the experimental difficulties of separating small amounts of iron from relatively large amounts of elements such as tin and antimony. These low results can hardly be attributed to any inherent weakness of the colorimetric method since no tendency of this sort is apparent in the other results obtained. Also, it is of interest to note that in the two cases where the Bureau reports analyses by a colorimetric method, the results obtained by the Ferron method checked the latter closer than the average value reported by the Bureau.

Summary

A study has been made of 7-iodo-8-hydroxyquinoline-5-sulfonic acid and its reaction with ferric ions. The solubility of the reagent has been determined in water, alcohol, acetic acid and in mixtures of these solvents. The color reaction has been investigated and a probable mechanism for it has been postulated. Cupric ions and salts that hydrolyze easily, or yield colored ions, interfere with the reaction and should not be present except in very low concentration. The sensitivity of the reaction has been determined. The reagent will measure quantitatively one part of iron in ten million parts of solution, when the observation is made in 50-ml. Nessler tubes (tall form). The color has been found to obey the Lambert–Beer law over the range of concentration examined. The effect of hydrogen-ion concentration has been studied and the optimum *p*H range for the color reaction determined. Aging and temperature have been found to have no effect on the color reaction. The optimum experimental conditions for the determination of iron have been established.

The iron content of a wide variety of materials has been determined colorimetrically, using 7-iodo-8-hydroxyquinoline-5-sulfonic acid. With one or two exceptions, the results obtained are in good agreement with the values reported by the National Bureau of Standards.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Condensations of Aromatic Amines with Formaldehyde in Media Containing Acid. V. Substituted Dihydroquinazolines from *p*-Chloroaniline and *p*-Bromoaniline

BY E. C. WAGNER AND ABNER EISNER[1]

The condensations of *p*-substituted amines with formaldehyde in aqueous acid solution have been studied for *p*-toluidine by Maffei and by the writers,[2] for *p*-phenetidine and *p*-nitroaniline by Maffei,[3] and by Cairncross and Bogert for *p*-aminobenzoic acid and ester[4] and for *p*-bromoaniline.[5] The reported products included the corresponding 3,6-disubstituted-3,4-dihydroquinazolines except in the case of *p*-bromoaniline, from which Cairncross and Bogert[5] obtained as the main product (19%) a base of m. p. 257° identified as 3-(*p*-bromophenyl)-6-bromo-3,4-dihydroquinazolone-4, and smaller amounts of two other bases (m. p. 204° and 193–196°), neither examined further. At the time these results were published the writers had practically completed a study of the condensation of *p*-chloroaniline with formaldehyde in dilute hydrochloric acid solution. The principal product was the expected substituted quinazoline. These contrasting results with two compounds so similar led to extension of the work to include *p*-bromoaniline. Condensation of this amine with formaldehyde in dilute hydrochloric acid solution at or below room temperature gave as the main product (26%) a base of m. p. 205.8° (corr.), found to be 3-(*p*-bromophenyl)-6-bromo-3,4-dihydroquinazoline. No base of m. p. 257° was isolated. Comparison of the two sets of conditions which yielded these unlike results shows that Cairncross and Bogert used less acid, more water, and considerably higher temperature (70°); the separation and purification of the several products involved a laborious and lengthy procedure. In the writers' experiments the isolation of the quinazoline offered no difficulty.

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[1] Present location: U. S. Bureau of Mines, Pittsburgh, Pa.

[2] (a) Lepetit and Maimeri, *Atti accad. Lincei,* [5] **26,** 558 (1917); (b) Lepetit, Maffei and Maimeri, *Gazz. chim. ital.,* **57,** 867 (1927); (c) Maffei, *ibid.,* **58,** 261 (1928); (d) Eisner and Wagner, THIS JOURNAL, **56,** 1938 (1934).

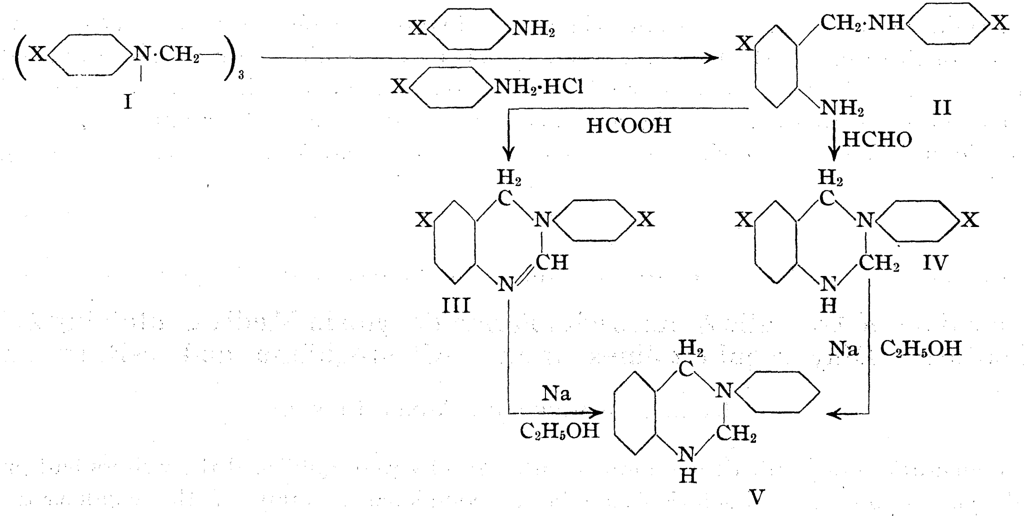
[3] Maffei, *Gazz. chim. ital.,* **59,** 3 (1929).

[4] Cairncross and Bogert, *Collection Czechoslov. Chem. Commun.,* **7,** 58 (1936).

[5] Cairncross and Bogert, *ibid.,* **7,** 548 (1936).

This paper describes the results of condensations of *p*-chloroaniline and of *p*-bromoaniline with formaldehyde in aqueous solutions containing hydrochloric acid, and the experiments by which the main reaction products were identified as the 3,6-disubstituted dihydroquinazolines. From both amines there were obtained also somewhat smaller amounts of lower-melting bases (135° and 134–135°, respectively), which have not been identified. The condensations were accompanied by methylation of part of the original amines, as has been reported also in the cases of *p*-toluidine and *p*-phenetidine.

The identifications of the substituted quinazolines were effected by the syntheses and transformations shown in the reaction scheme.



In the case of each starting compound (*p*-chloroaniline and *p*-bromoaniline) the trimeric Schiff base (I), prepared by the method of Miller,[6] was converted to the aminobenzylarylamine base (II) by the customary procedure,[7] and II was changed to the dihydroquinazoline (III) by ring-closure with formic acid.[7b] The dihydroquinazolines thus obtained were found to be identical with the main products of the condensations of the halogenated amines with formaldehyde. The structure of II, upon which the proof depends, may be inferred from the method of preparation used, and was supported by the characteristic behavior of the compound with formaldehyde to yield the tetrahydroquinazoline (IV), by the fact that II gave with benzaldehyde a monobenzal derivative from which benzaldehyde was split out by acid hydrolysis, and by the analytical values obtained for II, its benzal derivative, and IV. Hydrogenation of III to IV, apparently a simple way to establish the relationship of the two, was not effected,[8] but III was treated with excess sodium and alcohol under conditions which detached halogen quantitatively,[9] by which treatment both dihydroquinazolines yielded the same product (V), namely, 3-phenyl-1,2,3,4-tetrahydroquinazoline.[10] Further the tetrahydroquinazoline (IV) from *p*-bromoaniline was dehalogenated by sodium and alcohol yielding V, identical with the compound obtained from the two halogenated dihydroquinazolines (III). In the cases of the bromine compounds (III and IV) the bromine split off was recovered as silver bromide and weighed, with results close to the theoretical.

The foregoing evidence, together with analytical values, identify the two condensation products as 3-(*p*-chlorophenyl)-6-chloro-3,4-dihydroquinazoline (m. p. 192°, corr.) and 3-(*p*-bromophenyl)-6-bromo-3,4-dihydroquinazoline (m. p. 205.8°, corr.). Apparently both compounds have been obtained previously as unidentified reaction products, *viz.*, a base of m. p. 188° from *p*-chloroaniline, reported in a German patent,[11] and the

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[6] Miller and Wagner, This Journal, **54**, 3703 (1932).

[7] (a) German Patent 105,797; *Friedl.*, **5**, 84; (b) v. Walther and Bamberg, *J. prakt. Chem.*, [2] **73**, 209 (1906).

[8] No method came to hand by which the 1,2-double bond could be hydrogenated without cleavage of halogen. Alcohol and a moderate amount of sodium split off part of the halogen, as found also by Paal and Koch [*J. prakt. Chem.*, [2] **48**, 554 (1893)]. Hydrogen under 30 pounds (2 atm.) pressure and in presence of Raney nickel was found, in trials with other dihydroquinazolines, to be ineffective. Hydrogen in presence of palladized calcium carbonate [Busch and Stöve, *Ber.*, **49**, 1063 (1916); ref. 5] removes halogen without hydrogenating the double bond.

[9] Drogin and Rosanoff, This Journal, **38**, 711 (1916).

[10] Busch, *J. prakt. Chem.*, [2] **53**, 420 (1896).

[11] German Patent 122,474; *Friedl.*, **6**, 82.

base of m. p. 204° obtained from *p*-bromoaniline by Cairncross and Bogert.[5]

Experimental

Condensation of *p*-Chloroaniline and *p*-Bromoaniline with Formaldehyde in Aqueous Acid Solution.—The amine (0.1 mole) was dissolved in 100 cc. of water and 18 cc. of concd. hydrochloric acid. To the cold solution was added 10 cc. of 37% formalin (0.12 mole), and the mixture was stirred. A white precipitate appeared after some minutes, and increased steadily, while the liquid and precipitate acquired a gradually deepening red color. The separated hydrochlorides were filtered off after several hours. The filtrate was allowed to stand at room temperature, with removal of the further precipitate when it had become considerable, and this was continued until the final precipitate was negligible (eight to eleven days). The combined crops of colored hydrochlorides were dissolved in boiling water, filtered hot, and while still hot (to prevent separation of hydrochloride) the solution was made alkaline. The precipitate of bases was stirred until well granulated, and was filtered cold and washed with water. The yield from *p*-chloroaniline was 9.9 g., and from *p*-bromoaniline 11.2 g. The crude product was crystallized from 95% alcohol. In each case there separated first a crystalline base only slightly soluble in cold alcohol. After recrystallization from alcohol the base from *p*-chloroaniline melted at 186–187°, obsd., and that from *p*-bromoaniline at 201°, obsd. These bases were the dihydroquinazolines. The mother liquors were diluted while hot, and on chilling gave a second product more soluble than the first. The base from *p*-chloroaniline, after recrystallization from dilute alcohol, melted at 135°, obsd., and that from *p*-bromoaniline at 134–135°, obsd. The yields from *p*-bromoaniline were 4.74 g. of the 201° base (25.9%) and 3.34 g. of the 134° base.

After removal of the crude hydrochlorides in an experiment with *p*-bromoaniline the final filtrate was made alkaline and was steam-distilled, yielding 1.38 g. of steam-volatile oil, which was examined by the Hinsberg–Kessler procedure. There were obtained 0.29 g. of primary amine derivative (m. p. 127°), 0.31 g. of secondary amine derivative (brown oil), and 0.27 g. of tertiary base (diazotization and coupling test negative) whose crystallization was not feasible, but which gave a picrate of m. p. 139°, found to be identical (mixed melting point test) with the picrate of dimethyl-*p*-bromoaniline.

3 - (*p* - Chlorophenyl) - 6 - chloro - 3,4 - dihydroquinazoline.—Colorless needles from alcohol slightly diluted; m. p. 187°, obsd., or 192°, corr.

Anal. Calcd. for $C_{14}H_{10}N_2Cl_2$: C, 60.67; H, 3.61; N, 10.11; Cl, 25.62; mol. wt., 277. Found: C, 60.71; H, 3.69; N, 9.96, 9.95; Cl, 25.47, 25.47; mol. wt. (benzene), 294, 295; (camphor), 268, 270. Picrate: small yellow needles from alcohol; m. p. 233°, obsd., or 239°, corr.

3 - (*p* - Bromophenyl) - 6 - bromo - 3,4 - dihydroquinazoline.—Small elongated prisms from slightly diluted alcohol; m. p. 201°, obsd., or 205.8°, corr.

Anal. Calcd. for $C_{14}H_{10}N_2Br_2$: C, 45.92; H, 2.73; N, 7.65; Br, 43.66; mol. wt., 366. Found: C, 46.11; H, 2.72; N, 7.60, 7.41, 7.44; Br, 43.59; mol. wt. (camphor), 380, 376. Picrate: small bright yellow needles from hot alcohol; m. p. 235°, obsd., or 242°, corr.

Trimeric Methylene-*p*-chloroaniline.—This compound was reported by Bischoff and Reinfeld,[12] who found the m. p. to be 157° and the molecular weight 437, but gave no analytical values. Specimens made for this work by the method of Miller,[6] and crystallized from ligroin, melted at 151°, obsd., a value not raised by another crystallization. This compound was examined further in order to make certain of its identity.

Anal. Calcd. for $(C_7H_6NCl)_3$: Cl, 25.44; mol. wt., 417.5. Found: Cl, 25.25, 25.22; mol. wt. (benzene), 422, 420.

Reduction by zinc dust and hot dilute sulfuric acid[6,13] split the compound into bases recognized by the Hinsberg–Kessler procedure to be primary, secondary and tertiary. The evidence given establishes the compound as the trimeric Schiff base, as claimed by Bischoff and Reinfeld.

In molten camphor this base gave molecular weight values of 287 and 290, indicating partial depolymerization at 175°, as with similar compounds studied previously.[6]

Trimeric Methylene-*p*-bromoaniline.—This compound, not previously reported, was prepared by the method of Miller.[6] The reaction mixture, at first kept in an ice-bath, deposited initially a solid product which soon became viscous, and on standing overnight set to an amorphous mass; 17.2 g. of *p*-bromoaniline gave 11.4 g. of crude product (61.7%). The base crystallized from ligroin or alcohol in long thin flexible needles clumped in loose bulky masses. The compound melted at 166° obsd., or 168.8°, corr., to a turbid liquid.

Anal. Calcd. for $(C_7H_6NBr)_3$: C, 45.68; H, 3.26; N, 7.61; mol. wt., 552. Found: C, 45.80; H, 3.38; N, 7.64, 7.54; mol. wt. (benzene), 563, 546. In molten camphor the molecular weight results were 378, 389 and 374, showing partial depolymerization at 175°.

Cleavage of 2.95 g. of the compound by reduction[6] gave 2.28 g. of steam-volatile oil, which by the Hinsberg procedure was shown to contain primary and secondary bases, and yielded also 0.48 g. of a solid tertiary base. This melted at 54–55°, and was found by mixed melting point test to be identical with dimethyl-*p*-bromoaniline (m. p. 54°). The picrates (m. p. 140–141°) also were identical.

N-(2-Amino-5-chlorobenzyl)-*p*-chloroaniline (II).—This aminobenzylarylamine was made[14] by heating a mixture of 10 g. of crude methylene-*p*-chloroaniline, 23 g. of *p*-chloroaniline hydrochloride, 50 g. of *p*-chloroaniline and 5 cc. of nitrobenzene for six hours at 80–90°. The mixture was made alkaline and all steam-volatile material was removed. The somewhat gluey residue in the flask was extracted with ligroin (70–90°), yielding a yellow granular product (8.9 g., or 46.5%). Several crystallizations from ligroin gave small imperfect prisms with a slight yellow tinge, and a good melting point of 92°, obsd., or 93°, corr.

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[12] Bischoff and Reinfeld, *Ber.*, **36**, 47 (1903).

[13] Wagner, THIS JOURNAL, **54**, 660 (1932).

[14] The procedure used was based on German Patent 105,797 (ref. 7) and will be reported in a later paper.

Anal. Calcd. for $C_{13}H_{12}N_2Cl_2$: C, 58.45; H, 4.49; N, 10.49; mol. wt., 267. Found: C, 58.67, 58.74; H, 4.45, 4.57; N, 10.34, 10.45; mol. wt. (camphor), 272, 265.

N-(2-Amino-5-bromobenzyl)-*p*-bromoaniline (II).—A mixture of 10.0 g. of methylene-*p*-bromoaniline, 10 g. of *p*-bromoaniline hydrochloride and 100 g. of *p*-bromoaniline was heated in an oil-bath at 85° for four hours.[14] After removal of *p*-bromoaniline by steam distillation, the crude product in the flask solidified on cooling. It was partially dried, dissolved in hot alcohol, and recovered in several crops by progressive dilution with water. The crude yield was 10.7 g., or 55.3%. After two crystallizations from ligroin the substance was crystalline, though still yellowish, and melted well at 116°, obsd., or 117.6°, corr.

Anal. Calcd. for $C_{13}H_{12}N_2Br_2$: C, 43.84; H, 3.37; N, 7.87; mol. wt., 356. Found: C, 44.08, 44.12; H, 3.51, 3.63; N, 7.59, 7.58, 7.63; mol. wt. (camphor), 340, 348.

The resinous material obtained from the alcoholic mother liquors was worked up and yielded a small amount of the picrate of 3-(*p*-bromophenyl)-6-bromo-3,4-dihydroquinazoline (m. p. 232°; identified by mixed m. p. test), a normal by-product of the main reaction, as shown by Simons.[15]

N-(2-Benzalamino-5-chlorobenzyl)-*p*-chloroaniline.—To 0.50 g. of 2-amino-5-chlorobenzyl-*p*-chloroaniline in 10 cc. of hot alcohol was added 0.5 cc. of benzaldehyde. The liquid soon set to a mass of crystals. Alcohol was then added in portions to the heated mixture until the product just dissolved. On cooling the filtered solution there separated 0.48 g. of needle-shaped crystals, and from the filtrate after concentration 0.06 g. more, a total yield of 80.6%. The benzal derivative melted at 137°, obsd., or 139°, corr. Heated with dilute sulfuric acid it yielded benzaldehyde.

Anal. Calcd. for $C_{20}H_{15}N_2Cl_2$: N, 7.89. Found: N, 7.80, 7.84.

N-(2-Benzalamino-5-bromobenzyl)-*p*-bromoaniline.—Prepared by the method described for the corresponding chlorine compound this derivative was obtained in 86.6% yield. After recrystallization from alcohol it melted at 142°, obsd., or 144.6°, corr.

Anal. Calcd. for $C_{20}H_{15}N_2Br_2$: N, 6.31. Found: N, 6.37, 6.27.

Conversion of Aminobenzylarylamine Bases (II) to the Corresponding Tetrahydroquinazolines (IV)

Ring-closure by introduction of the methylene group was effected by formaldehyde in alcohol containing potassium hydroxide, as described previously.[2d,16]

3-(*p*-Chlorophenyl)-6-chloro-1,2,3,4-tetrahydroquinazoline.—This compound was obtained as small needles and in 72.7% yield. After crystallization from slightly diluted alcohol it melted at 155°, obsd., or 158° corr.

Anal. Calcd. for $C_{14}H_{12}N_2Cl_2$: N, 10.00. Found: N, 9.92, 10.03, 9.85.

3-(*p*-Bromophenyl)-6-bromo-1,2,3,4-tetrahydroquinazoline.—The yield of small plates was 92.9%; m. p. 170°, obsd., or 173°, corr. Recrystallization from hot alcohol appeared to deteriorate this compound both in appearance and melting point; better results were obtained when alcohol containing a small amount of potassium hydroxide was used.[17]

Anal. Calcd. for $C_{14}H_{12}N_2Br_2$: N, 7.61. Found: N, 7.67, 7.59.

Conversion of Aminobenzylarylamines (II) to the Corresponding Dihydroquinazolines (III)

Ring closure through =CH— was effected by heating the base with 90% formic acid on the water-bath.[7b] The mixture was made alkaline with sodium hydroxide, and steam-volatile material was removed. The residue was dried, and resins were dissolved by extraction with a little ether in a beaker, assisted by manipulation with a stirring rod with flattened end. The crystalline mass of nearly white dihydroquinazoline was filtered off, washed with a little chilled ether, and recrystallized from slightly diluted alcohol.

3-(*p*-Chlorophenyl)-6-chloro-3,4-dihydroquinazoline was thus obtained from aminochlorobenzyl-*p*-chloroaniline as fine needles; after crystallization from alcohol the base melted at 186–187°, obsd. Mixed with the base of m. p. 187°, obsd., obtained by the *p*-chloroaniline-formaldehyde condensation, the m. p. was 186–187°, obsd.

3-(*p*-Bromophenyl)-6-bromo-3,4-dihydroquinazoline was obtained, after crystallization from alcohol, as a yellow-tinted crystal meal of m. p. 200°, obsd. Mixed with the base of m. p. 202°, obsd., obtained from the condensation of *p*-bromoaniline and formaldehyde the compound melted at 201°, obsd.

Hydrogenation of the Halogenated Dihydroquinazolines

Saturation of the 1,2-double bond, and replacement of halogen by hydrogen, were effected in one operation by drastic reduction with sodium and absolute alcohol, using for 0.5 g. of the dihydroquinazoline about 2.5 g. of sodium and 25 cc. of alcohol. After the sodium had dissolved water was added and the alcohol was taken off under reduced pressure. The precipitated solid was crystallized from dilute alcohol. Both the chlorine and bromine compounds (III) gave the same product: colorless needles of m. p. 121–122°; a mixture of the two had the same melting point. In an experiment with 3-bromophenyl-6-bromodihydroquinazoline the bromine was recovered and weighed as AgBr: 0.50 g. of dihydroquinazoline gave 0.51 g. of silver bromide, corresponding to 43.4% bromine, that calculated being 43.7%. The product, 3-phenyl-3,4-dihydroquinazoline (V), made synthetically by Paal and Busch,[16,18] was reported to melt at 119°.

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.67; N, 13.33; mol. wt., 210. Found: C, 79.82; H, 6.64; N, 13.21, 13.36, 13.33; mol. wt. (camphor), 211, 218.

Debromination of 3-(*p*-Bromophenyl)-6-bromo-1,2,3,4-tetrahydroquinazoline.—Treatment with sodium and alcohol as outlined above gave from 0.50 g. of this compound

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[15] Simons, This Journal, **59**, 518 (1937).

[16] Busch and Dietz, *J. prakt. Chem.*, [2] **53**, 420 (1896).

[17] The relative instability of the structural condition >N—CH_2—N< in acid media is familiar. A striking example is afforded by the conversion of bis-(*p*-anisyl)-methane to the trimeric Schiff base on crystallization from alcohol.[12]

[18] Paal and Busch, *Ber.*, **22**, 2693 (1889).

0.20 g. of fine needles of m. p. 118°, obsd. A mixture of the product with that obtained by similar treatment of the dihydroquinazoline (m. p. 121°) melted well at 120°. The bromine split out was weighed as silver bromide: 0.50 g., corresponding to 42.6% bromine, that calculated being 43.5%.

Grateful acknowledgment is made to the Faculty Research Committee of the University of Pennsylvania for a grant to aid this study, and to the following for most of the analytical results reported: W. S. Young (molecular weights), F. W. Landau (nitrogen), and Wm. McClellan (carbon and hydrogen).

Summary

Condensation of *p*-chloroaniline and of *p*-bromoaniline with formaldehyde in cold aqueous solution containing hydrochloric acid yielded as main products the corresponding 3-(halogenophenyl)-6-halogeno-3,4-dihydroquinazolines, of m. p. 192° (corr.) and m. p. 206° (corr.), respectively. The identities of these bases were experimentally established. Formation of these products was accompanied by that of unidentified bases and by methylation of part of the original amines.

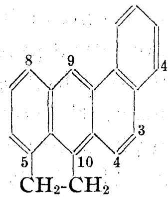
Philadelphia, Penna. Received March 1, 1937

[Contribution from the Chemical Laboratory of Harvard University]

4,10-Ace-1,2-benzanthracene

By Louis F. Fieser and Arnold M. Seligman

The powerfully carcinogenic hydrocarbon cholanthrene[1,2] is the 5,10-ace- (or dimethylene-) derivative (I) of 1,2-benzanthracene and it is one of four possible ace- derivatives of this hydrocarbon. Two of the remaining isomers already have been synthesized and submitted to biological tests. The 8,9-ace- compound (8,9-dimethylene-1,2-benzanthracene[2]) has carcinogenic properties, but it produces tumors less than half as rapidly as cholanthrene.[3] The 3,4′-isomer (acenaphthanthracene[4]), in which both meso positions are unsubstituted, has given only negative results.[5] The synthesis of the fourth isomer, 4,10-ace-1,2-benzanthracene (VIII, below), is described in the present paper. The hydrocarbon is of particular interest because of the indications that substitution at the 10-position in the 1,2-benzanthracene molecule often is particularly favorable for the development of cancer-producing properties,[6] but tests with the new hydrocarbon which are being conducted by Dr. M. J. Shear are not yet complete. The compound produces severe ulceration in mice as rapidly as cholanthrene, but thus far no tumors have been obtained. It is interesting that the three isomeric ace-1,2-benzanthracenes in which the five-membered ring is joined to a meso position of the aromatic system all show some biological activity, while the 3,4′-isomer is completely inactive.



I

The initial step in the synthesis consisted in the condensation of hydrindene with succinic anhydride. As in other Friedel and Crafts reactions, substitution occurred exclusively in the β-position, giving β-(5-hydrindoyl)-propionic acid (II). Reduction to III, cyclization, and reduction to V all proceeded smoothly, and the structure of the tricyclic compounds was established by oxidation of the ketone IV to pyromellitic acid. The structure of the keto acid II follows from that of the ketone. The condensation of 6,7-cyclopentenotetralin (V) with benzoyl chloride gave a liquid product for which only the structure VI is possible, and dehydrogenation of the ketone with selenium gave a liquid of approximately the composition of 1-benzoyl-2,3-cyclopentenonaphthalene, VII. The final step in the synthesis consists in a modified Elbs condensation of the type employed for the preparation of methyl-

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(1) Cook, Haslewood and Robinson, *J. Chem. Soc.*, 667 (1935); Cook and Haslewood, *ibid.*, 767, 770 (1935).

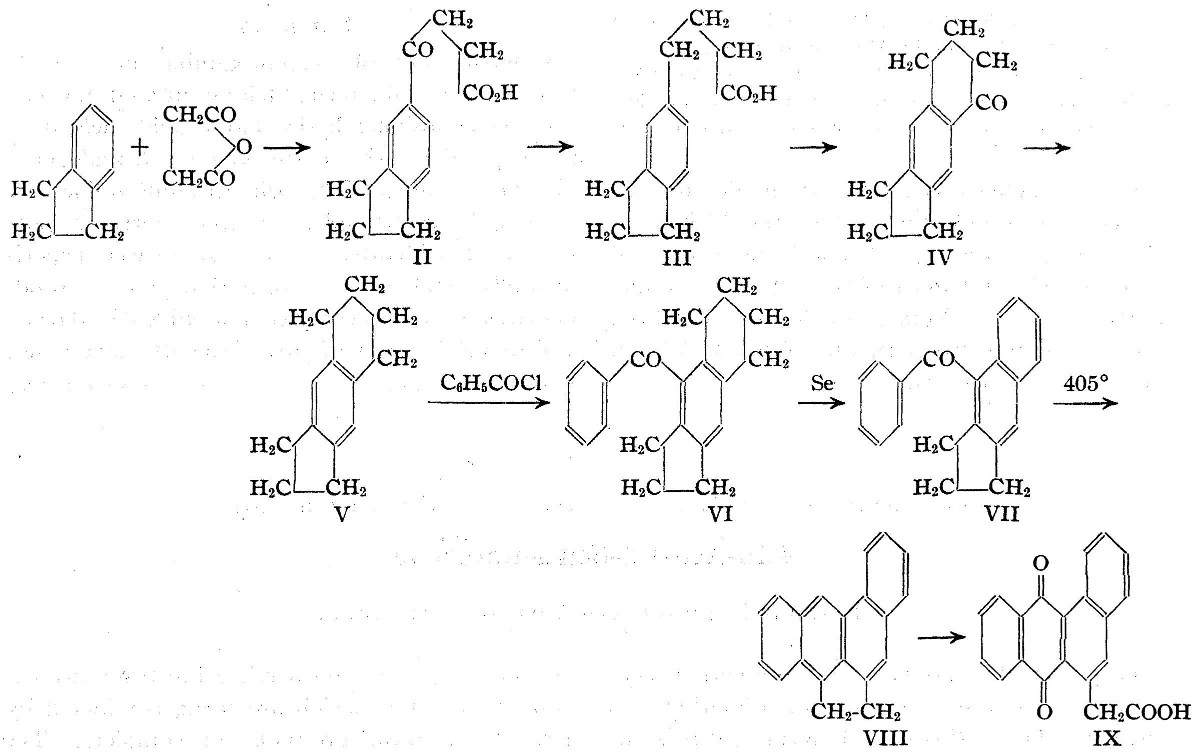
(2) Fieser and Seligman, This Journal, **57**, 2174 (1935).

(3) Shear, *Am. J. Cancer*, **28**, 334 (1936).

(4) Nicodemus, Eng. Patent 251,270 (1926), Ger. Patent 481,819 (1929); Nicodemus and Berndt, U. S. Patent 1,776,925 (1930); Cook, *J. Chem. Soc.*, 1087 (1930); Geyer and Zuffanti, This Journal, **57**, 1787 (1935).

(5) Cook, *Proc. Roy. Soc.* (London), **B111**, 495 (1932).

(6) L. F. Fieser, Mary Fieser, Hershberg, Newman, Seligman and Shear, *Am. J. Cancer*, **29**, 260 (1937).



cholanthrene,[7] but since the ring closure in this case involves substitution in a phenyl, rather than a naphthyl, nucleus, it is not surprising that the hydrocarbon VIII, isolated as the picrate from the oily product of pyrolysis, was obtained in only 10% yield. No difficulty was experienced, however, in obtaining the 4,10-ace-1,2-benzanthracene in a pure condition. Confirmatory evidence of the structure was found in the oxidation of the hydrocarbon to an anthraquinone acetic acid corresponding in properties and analysis to formula IX.

The pyrolysis of the hydrogenated ketone VI also was investigated in order to determine if there is any preference for the participating of the five-membered or six-membered ring in the cyclization. One reaction product was obtained easily in a crystalline and highly pure condition on treating the oily distillate with ether, and a second compound was isolated from the mother liquor through the picrate. The latter compound is a hydrocarbon of the expected composition ($C_{20}H_{18}$), and, as it yielded 4,10-ace-1,2-benzanthracene (VIII) on dehydrogenation, it evidently is the normal product of a cyclization utilizing the cyclopenteno ring, and it can be assigned the formula X. The hydrocarbon which crystallizes from ether has two atoms of hydrogen less than X, or than the hypothetical pyrolysis product XI, and it is resistant to dehydrogenation with selenium. On oxidation, the compound was found to yield the known phenanthrene-8,9-dicarboxylic anhydride, XIII.[8] The hydrocarbon therefore is an 8,9-substituted phenanthrene derivative, and the most probable structure is that of formula XII. The exact location of the alicyclic double bond has not been established. The hydrocarbon evidently is formed as the result of an intramolecular cyclization involving a methylene group of the cyclohexeno ring of the ketone VI, but the anthracene derivative XI, which would result as the primary product of this condensation, does not appear to be stable at the temperature of the reaction. A stabilization possibly is achieved by the migration of one double bond into the angular six-membered ring, followed by the aromatization of this ring through a process of disproportionation, one of the double bonds in the originally aromatic ring remaining at the position between two bridge heads.

That the cyclodehydration proceeds in both possible directions is in keeping with a similar observation[9] concerning a ketone having available for the condensation both an adjacent cyclo-

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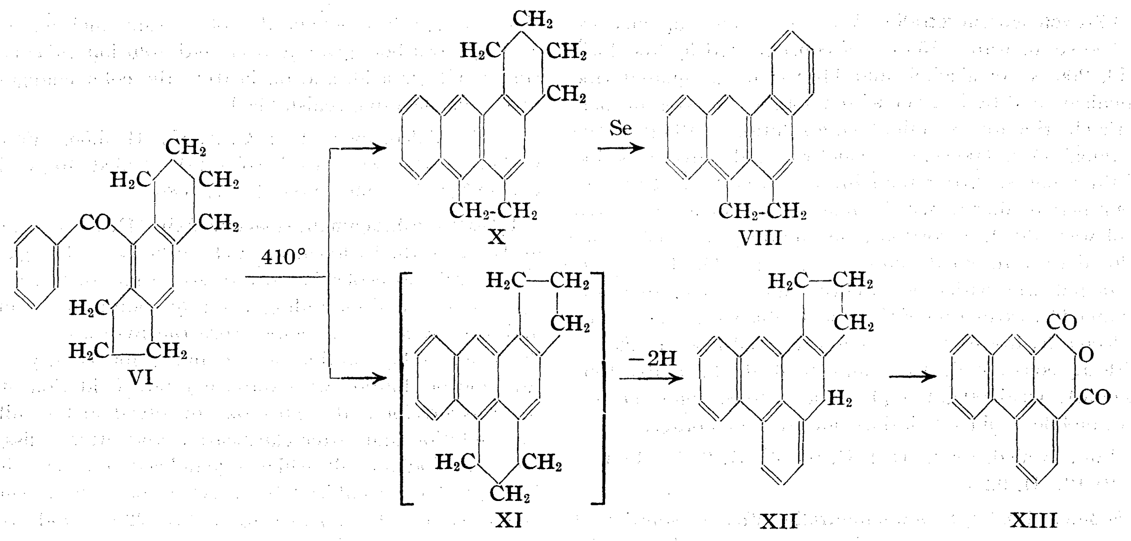
[7] Fieser and Seligman, THIS JOURNAL, **57**, 228, 942 (1935); **58**, 2482 (1936).

[8] Pschorr, *Ber.*, **39**, 3115 (1906).

[9] Fieser and Hershberg, THIS JOURNAL, **59**, 394 (1937).



penteno ring and an *o*-methyl group. The present results find a correlation also with observations concerning the pyrolysis of tetralyl naphthyl ketones,[10] for in two cases phenanthrene derivatives were obtained in place of the expected anthracenoid isomers, and in one instance a dehydro compound was isolated. The controlling factor doubtless is that the angular arrangement of three aromatic rings presents a more stable structure than the linear arrangement, and it is interesting that a readjustment of double bonds and hydrogen atoms occurs without the use of catalysts at the temperature of the pyrolysis.

We are indebted to Mr. Philip A. Shaffer, Jr., for able assistance in the preparative work.

Experimental Part[11]

β-(5-Hydrindoyl)-propionic Acid (II).—The hydrindene employed, b. p. 79.0° (29 mm.), was prepared and carefully fractionated in conjunction with Dr. T. L. Gresham. To a solution of 118 g. of the pure hydrocarbon and 110 g. of succinic anhydride in 500 cc. of tetrachloroethane and 200 cc. of nitrobenzene, cooled to 0°, 270 g. of aluminum chloride was added in portions. The mixture was cooled in an ice-bath for several hours, allowed to stand at room temperature for two days, and then poured onto ice and hydrochloric acid. After removing the solvents with steam, the product was taken into soda solution, and precipitated after clarification with Norite. The crude acid, m. p. 118–120°, uncorr., was satisfactory for use in the next step; yield, 211 g. (97%). After several crystallizations from dilute alcohol and from benzene, the substance was obtained as small needles, m. p. 125–125.5°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.52; H, 6.47. Found: C, 71.70; H, 6.55.

γ-(5-Hydrindyl)-butyric Acid (III).—Following the general procedure of Martin,[12] a mixture of 211 g. of the acid II, 750 g. of amalgamated mossy zinc, 600 cc. of concentrated hydrochloric acid, 300 cc. of water, and 600 cc. of toluene was refluxed for fifty hours, with the addition of 500 cc. of concentrated acid at intervals. The toluene layer was washed, clarified and distilled, the product being collected as a colorless distillate, b. p. 202° (5 mm.), m. p. 55°; yield, 145 g. (73%). The acid crystallizes from alcohol as colorless needles melting at 54.9–55.2°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.43; H, 7.90. Found: C, 76.50; H, 8.13.

6,7-Cylopenteno-1-tetralone (IV).—The acid III (145 g.) was refluxed with 200 cc. of thionyl chloride for several hours, and the acid chloride was obtained as a colorless liquid, b. p. 170° (10 mm.); yield, 143 g. (90%). A solution of this material in 250 cc. of carbon bisulfide was added during one hour to a stirred suspension of 130 g. of aluminum chloride in 2 liters of carbon bisulfide at 0°. After being stirred at 0° for one and one-half hours, the mixture was allowed to stand at room temperature for several hours and then decomposed with ice and acid. After removing the solvent with steam, the residual oil was extracted with ether, dried, and distilled. The ketone was obtained as a colorless liquid, b. p. 151–152° (2 mm.); yield, 110.5 g. (92%, based on the acid chloride used). The sample darkened on long standing.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.27, 83.74; H, 7.47, 8.25.

In order to establish the structure, 5 g. of the ketone was heated with 1.5 cc. of concentrated nitric acid and 2.5 cc. of water at 190° for fourteen hours; 1.5 cc. of concentrated acid was added and the heating continued for twelve hours. On concentrating the solution, adding fuming nitric acid, and cooling, 0.7 g. of pyromellitic acid separated. The material was converted into the anhydride at 250°, and this was sublimed and crystallized from dioxane as in a previous experiment.[13] The anhydride melted at 282–283° and did not depress the melting point of an authentic sample.

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[10] Fieser and Seligman, THIS JOURNAL, **58**, 478 (1936).

[11] Melting points are corrected unless otherwise noted. Analyses by Mrs. G. M. Wellwood.

[12] Martin, THIS JOURNAL, **58**, 1438 (1936).

[13] Fieser and Hershberg, *ibid.*, **57**, 2196 (1935).

6,7-Cyclopentenotetralin (V).—To a refluxing mixture of 350 cc. of water, 750 cc. of concentrated hydrochloric acid, 200 cc. of alcohol, and 1100 g. of granulated zinc (amalgamated by contact with a solution of 56 g. of mercuric chloride for five minutes), a solution of 109 g. of the tetralone IV in 300 cc. of alcohol was added over a period of three hours. After refluxing for an additional twelve-hour period, during which time 400 cc. of concentrated acid was added in portions, the mixture was cooled and diluted with an equal volume of water. The liquor was extracted twice with ether, and the bulk of the product was obtained by extraction of the zinc residue with ether. The collected hydrocarbon was steam distilled from a mixture with aqueous alkali, dried, and distilled; b. p. 104–106° (3 mm.); yield, 90 g. (89%). The hydrocarbon is a colorless, mobile liquid which does not alter on storage.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.66; H, 9.37. Found: C, 91.12; H, 9.23.

5-Benzoyl-6,7-cyclopentenotetralin (VI).—A solution of 90 g. of V in 100 cc. of tetrachloroethane was added in the course of one-half hour to a stirred mixture of 80 g. of benzoyl chloride, 90 g. of aluminum chloride, 400 cc. of tetrachloroethane, and 100 cc. of nitrobenzene at 0°. After standing overnight, the mixture was decomposed with 1.5 kg. of ice and 150 cc. of concentrated hydrochloric acid, the solvent was removed with steam, and the residual oil was washed in ethereal solution with water and alkali, dried, and distilled. The ketone was obtained as a very viscous, pale yellow oil, b. p. 183–185° (0.5 mm.) or 215–217° (3.5 mm.); yield, 130 g. (90%).

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.90; H, 7.30. Found: C, 87.04, 86.30; H, 7.76, 7.49.

1-Benzoyl-2,3-cyclopentenonaphthalene (VII).—The above ketone (20 g.) was heated with an equal weight of selenium in an atmosphere of nitrogen at 290° (bath) for twenty-four hours, adding 20 g. of fresh selenium in portions at eight-hour intervals. The material was extracted with benzene and the dark solution was filtered, shaken with a few drops of mercury, allowed to stand overnight, treated with Norite, filtered, and distilled. The product was a yellow, viscous oil, b. p. 215–220° (1.5 mm.); yield, 13.5 g. (69%). The analyses indicate that the material probably contained a small amount of the more highly hydrogenated ketone.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.32, 88.26; H, 6.89, 7.12.

Dehydrogenation of VI with sulfur was investigated without success.

4,10-Ace-1,2-benzanthracene (VIII).—The above oil (13.5 g.) was heated in a bath at 405° for forty-five minutes, and on distillation at 2 mm. pressure there was obtained a viscous yellow oil which failed to solidify or to yield crystals from ether. A hydrocarbon picrate was obtained without difficulty from benzene–ether solution; 5.5 g. of crystalline picrate was collected, and on purification the substance formed clusters of brown-black needles melting at 148–149°. The hydrocarbon recovered from the purified picrate crystallized from ether in the form of stout yellow needles melting at 138.5–140°; yield, 1.3 g. (10%). Further purification by passage through an adsorption tower of alumina and crystallization gave faintly yellow needles of the same melting point. The hydrocarbon gives a deep red solution in concentrated sulfuric acid, and on heating the color changes to violet and then to greenish-black.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.17; H, 5.88. *Anal.* (picrate). Calcd. for $C_{20}H_{14}\cdot C_6H_3O_7N_3$: N, 8.69. Found: N, 8.80.

1,2-Benzanthraquinone-4-acetic Acid (IX).—A solution of 0.35 g. of the hydrocarbon VIII in 20 cc. of hot glacial acetic acid was cooled rapidly to give a fine suspension of the material, and on adding 1.8 g. of sodium dichromate and shaking at room temperature the hydrocarbon soon dissolved. The solution was refluxed for twenty minutes and on dilution with water a yellow oxidation product was precipitated. This was dissolved in hot, dilute soda solution and, after clarification and after redissolving some sodium salt which crystallized, reprecipitated. The quinone crystallized from xylene–benzene as small, yellow needles (0.2 g.) melting at 228–229.5° and giving an orange-red vat with alkaline hydrosulfite solution.

Anal. Calcd. for $C_{20}H_{12}O_4$: C, 75.92; H, 3.83. Found: C, 75.81; H. 3.80.

Pyrolysis of 5-Benzoyl-6,7-cyclopentenotetralin.—After heating 13.5 g. of the ketone for one hour at 410°, the residue was distilled in vacuum and the viscous oil obtained was warmed with ether. Before the bulk of the material had dissolved, a crystalline product began to separate, and this substance (A, see below) was easily obtained in a nearly pure condition, m. p. 140–141°, uncorr.; yield, 2.1–2.5 g. (17–21%). After removing this hydrocarbon as completely as possible, the oil recovered from the mother liquor was treated with picric acid in benzene–ether solution, and on standing there was obtained 2.5 g. of a crystalline picrate melting at about 110°. Further crystallization from benzene gave 1 g. (4%) of pure tetrahydro-4,10-ace-1,2-benzanthracene picrate, which formed small, dark red plates melting at 131–132°. The corresponding hydrocarbon is described below.

In one experiment 13.5 g. of ketone was heated as above except for the addition of 1.3 g. of zinc dust. There was little change in the yields, 1.8 g. of hydrocarbon and 3 g. of crude picrate being obtained.

Hydrocarbon A, Probably Δ^3-Dehydro-3,4-trimethylene-isobenzanthrene-2 (XII).—The pyrolysis product separating easily from ether was purified by further crystallization from this solvent and by chromatographic adsorption. It forms faintly yellow-green, fluorescent prisms melting at 144.5–145°. Its solution in sulfuric acid is red, changing to a darker red on heating without showing signs of decomposition. The picrate crystallizes from benzene–ether in the form of crimson needles melting at 136–137°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.68, 93.89; H, 6.34, 6.49. *Anal.* (picrate). Calcd. for $C_{20}H_{16}\cdot C_6H_3O_7N_3$: N, 8.95. Found: N, 9.12.

On attempting to dehydrogenate the hydrocarbon (0.6 g.) with selenium (2 g.) at 295° for twenty-four hours, considerable material was destroyed and the only product isolated was unchanged starting material (0.1 g.).

Oxidation was effected by refluxing a solution of 2 g. of the hydrocarbon and 16 g. of sodium dichromate in 50 cc.

of glacial acetic acid for one-half hour. Yellow needles of the reaction product began to separate from the boiling solution, and the precipitation was completed by the addition of water. The crude oxidation product was dissolved in dilute sodium hydroxide solution at the boiling point and the yellow solution was filtered from a dark sludge of suspended material. When refiltered through a pad of charcoal, the solution was nearly colorless, and on adding acid and boiling, the product separated as a pale yellow precipitate in a nearly pure condition; yield 0.5 g. The substance is insoluble in cold alkali. On crystallization from dioxane, in which it is readily soluble, the substance formed fan-shaped clusters of pale yellow needles, m. p. 280.5–281.5°.

Anal. Calcd. for $C_{16}H_8O_3$: C, 77.41; H, 3.25. Found: C, 77.71; H, 3.39.

The analysis and properties are those of phenanthrene-8,9-dicarboxylic anhydride, for which Pschorr[8] reports the corrected melting point 283–284°. No depression was observed in the melting point on admixture with a slightly less pure sample of the anhydride previously prepared in this Laboratory.[14]

1',2',3',4'-Tetrahydro-4,10-ace-1,2-benzanthracene (X).—This hydrocarbon was recovered from the purified picrate, m. p. 131–132°, described above, by distribution between ammonia water and ether. The compound crystallizes well when an ethereal solution is diluted with methanol and concentrated to the point of saturation. The sample for analysis was distilled in vacuum and recrystallized, forming silky, colorless needles melting at 106–107°. The solutions are beautifully fluorescent.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.69; H, 7.24. *Anal.* (picrate). Calcd. for $C_{20}H_{18} \cdot C_6H_3O_7N_3$: N, 8.62. Found: N, 8.78.

Dehydrogenation of the hydrocarbon with a large excess of selenium was conducted at 300–320° for twenty hours. The product was extracted with benzene, the solution was passed through a tower of alumina, and the recovered material on crystallization from methanol gave pale yellow needles melting at 135–137° and showing no depression when mixed with 4,10-ace-1,2-benzanthracene.

Summary

The synthesis of 4,10-ace-1,2-benzanthracene, an isomer of the carcinogenically active cholanthrene, has been accomplished by the use of the modified Elbs reaction. This pyrolytic reaction, applied in another case where both a five-membered and a six-membered ring are available for condensation, was found to proceed in both possible directions. Further evidence was found of the tendency of 1,9-trimethylene derivatives of anthracene to undergo transformation to phenanthrene derivatives in the course of the pyrolysis.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 17, 1937

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[14] Fieser and Peters, THIS JOURNAL, **54**, 4373 (1932).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Tautomerism of Certain Derivatives of Acetomesitylene

BY E. P. KOHLER AND R. B. THOMPSON

In a recent study of the structure of the magnesium derivatives of mono ketones[1] it was found that the derivative of benzhydryl acetomesitylene is an enolate and that the corresponding enol is sufficiently persistent in solution to be detectable as peroxide. This observation is important because at present the only reliable evidence that a substance obtained by adding a metallic derivative to an unsaturated ketone or ester is an enolate, is its conversion into an enol by a process which does not enolize the corresponding ketone or ester.

It was found, also, that in a series of related mono ketones the mode of acylation of the magnesium derivatives appeared to be associated with the relative persistence of the enolic modifications. At the time this observation was made it was not possible to study the behavior of these enolates in reactions involving alkylation because they failed to react with any of the alkylating agents that were available. Having found, in the meanwhile, that magnesium derivatives of this type react very readily with chloromethyl ether we have now compared the mode of alkylation of the enolates which differed most in the mode of acylation, namely, the magnesium derivatives of benzhydryl acetophenone and benzhydryl acetomesitylene. We have also compared the tautomerism of a number of other ketonic derivatives of mesitylene with that of the corresponding derivatives of benzene. The results are embodied in the present paper.

When the magnesium derivative of benzhydryl acetophenone reacts with chloromethyl ether the result is a mixture composed of 30% of the

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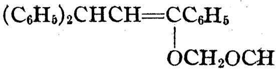
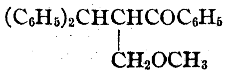
[1] Kohler, Tishler and Potter, THIS JOURNAL, **57**, 2517 (1935).

O-alkylation product I and 70% of the C-alkyl derivative II.



$(C_6H_5)_2CHCH{=}\underset{OCH_2OCH_3}{C}C_6H_5$

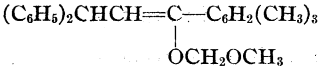
I



$(C_6H_5)_2CH\underset{CH_2OCH_3}{C}HCOC_6H_5$

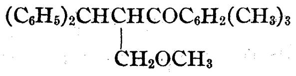
II

The magnesium derivative of benzhydryl acetomesitylene likewise yields both O- and C-alkyl derivatives but the relative amounts are almost completely reversed, at least 75% of the product being the O-alkyl derivative, III. In these two



$(C_6H_5)_2CHCH{=}\underset{OCH_2OCH_3}{C}{-}C_6H_2(CH_3)_3$

III

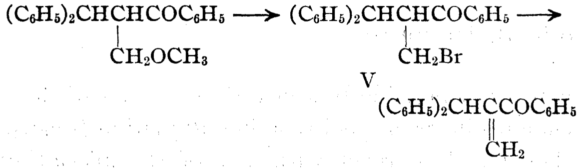


$(C_6H_5)_2CH\underset{CH_2OCH_3}{C}HCOC_6H_2(CH_3)_3$

IV

cases, therefore, alkylation and acylation follow the same course, both being associated in some manner with the persistence of the enolic form.

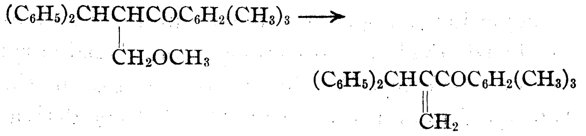
The O-alkylation products I and III are of little interest because their behavior is similar to that of all other acetals. The more interesting C-alkyl derivatives differ considerably in their chemical properties. Thus the benzene derivative II is insensitive both to bases and to dilute acids. In order to convert it into an unsaturated ketone it is necessary to replace the methoxyl group with bromine by prolonged heating with concentrated hydrobromic acid and then to eliminate hydrogen bromide from the bromo compound



$(C_6H_5)_2CH\underset{CH_2OCH_3}{C}HCOC_6H_5 \longrightarrow (C_6H_5)_2CH\underset{CH_2Br}{C}HCOC_6H_5 \longrightarrow (C_6H_5)_2CH\underset{CH_2}{\overset{}{C}}COC_6H_5$

V VI

In contrast both methyl alcoholic potassium hydroxide and acids convert the mesitylene derivative IV directly into the corresponding unsaturated ketone

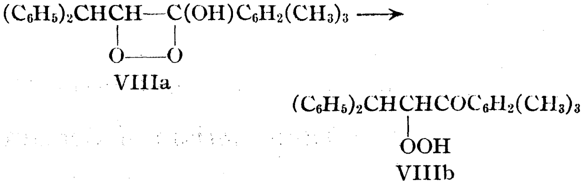


$(C_6H_5)_2CH\underset{CH_2OCH_3}{C}HCOC_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2CH\underset{CH_2}{C}COC_6H_2(CH_3)_3$

VII

The properties of these C-alkylation products, like the behavior of the magnesium enolates toward acylating and alkylating agents, show that in ketones containing the group $—CHCOC_6H_2(CH_3)_3$ the mesitylene residue increases the activity of the α-hydrogen atoms, promotes enolization and enhances the stability of the enolic form. Although this form of benzhydryl acetomesitylene could not be isolated, we secured ample evidence of its presence and persistence in solutions obtained by acidifying its magnesium derivative. These solutions do not give a color reaction with ferric chloride—doubtless because the enol lacks the oxygen necessary for chelation[2]—but they decolorize bromine instantaneously and a titration by the Kurt Meyer method showed that they still contained about 90% of enol after several hours in a freezing mixture. They also absorb oxygen avidly, but when they are concentrated to the point of crystallization they deposit only the ketonic form which neither decolorizes bromine nor combines with oxygen.

As a result of autoxidation the enol is converted into a crystalline peroxide which differs, structurally, from all other substances of this type in that it has hydrogen in place of the usual hydrocarbon residue in the α position. In view of this peculiarity it is necessary to consider the possibility that the cyclic peroxide which would be expected may immediately undergo rearrangement to an open chained isomer



$(C_6H_5)_2CH\underset{O}{C}H{-}\underset{O}{C}(OH)C_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2CH\underset{OOH}{C}HCOC_6H_2(CH_3)_3$

VIIIa VIIIb

In thermal stability and chemical activity the peroxide does not differ materially from known peroxides which are undoubtedly cyclic in structure. When it is heated it decomposes, with a flash, into mesitylene carbonic acid and diphenyl acetaldehyde. It readily loses one atom of oxygen to hydrogen iodide and to platinum and hydrogen, being reduced to a hydroxy ketone instead of to the usual oxanol. Like the peroxides of known structure, also, it is attacked by aqueous alkalies, but instead of being cleaved it is dehydrated to an α-diketone. All of these properties and products can be reconciled with either of the two formulas, but the peroxide is neutral while all known derivatives of hydrogen peroxide, including the naphthalene derivative discovered by Hock and Susemihl,[3] are distinctly acidic. It seems probable, therefore, that the substance is

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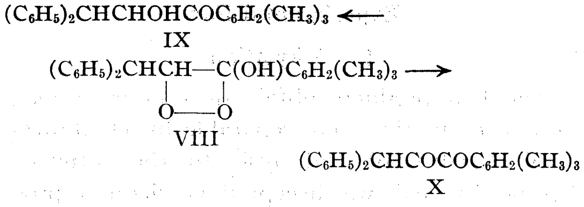
(2) Hantzsch, *Ann.*, **392**, 292 (1912).

(3) Hock and Susemihl, *Ber.*, **66**, 61 (1933).

a cyclic peroxide, that the divergent reduction product is due to the instability of the oxanol[4] and that aqueous alkali rearranges the cyclic to the open chained form which is then dehydrated to the diketone



$$(C_6H_5)_2CHCHOHCOC_6H_2(CH_3)_3 \longleftarrow$$

IX

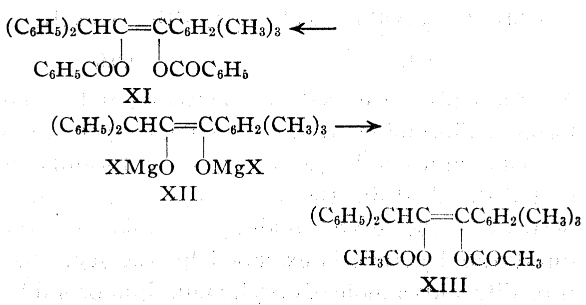
$$(C_6H_5)_2CH\underset{\underset{\textstyle O}{|}}{C}H-\underset{\underset{\textstyle O}{|}}{C}(OH)C_6H_2(CH_3)_3 \longrightarrow$$

VIII

$$(C_6H_5)_2CHCOCOC_6H_2(CH_3)_3$$

X

Although not perceptibly enolized in solution, the hydroxy ketone IX, like all other substances containing the group $CHCOC_6H_2(CH_3)_3$, is converted into an enolate by Grignard reagents. It liberates two moles of gas from methyl magnesium iodide and when the resulting magnesium compound is acylated the product is a di-ester



$$(C_6H_5)_2CH\underset{\underset{\textstyle C_6H_5COO}{|}}{C}=\underset{\underset{\textstyle OCOC_6H_5}{|}}{C}C_6H_2(CH_3)_3 \longleftarrow$$

XI

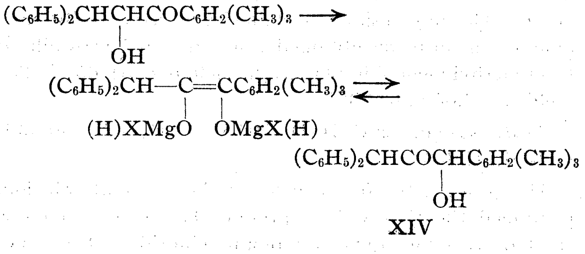
$$(C_6H_5)_2CH\underset{\underset{\textstyle XMgO}{|}}{C}=\underset{\underset{\textstyle OMgX}{|}}{C}C_6H_2(CH_3)_3 \longrightarrow$$

XII

$$(C_6H_5)_2CH\underset{\underset{\textstyle CH_3COO}{|}}{C}=\underset{\underset{\textstyle OCOCH_3}{|}}{C}C_6H_2(CH_3)_3$$

XIII

Evidently the magnesium derivative is a di-enolate which undergoes only O-acylation. The corresponding di-enol could not be isolated. Like the enol of benzhydryl acetomesitylene it is remarkably persistent in solution but when these solutions are concentrated they deposit only the isomeric hydroxy ketone



$$(C_6H_5)_2CH\underset{\underset{\textstyle OH}{|}}{C}HCOC_6H_2(CH_3)_3 \longrightarrow$$

$$(C_6H_5)_2CH-\underset{\underset{\textstyle (H)XMgO}{|}}{C}=\underset{\underset{\textstyle OMgX(H)}{|}}{C}C_6H_2(CH_3)_3 \rightleftarrows$$

$$(C_6H_5)_2CHCO\underset{\underset{\textstyle OH}{|}}{C}HC_6H_2(CH_3)_3$$

XIV

In this case, therefore, it is possible to follow, step by step, the isomerization of an hydroxy ketone by way of an intermediate di-enol. This same di-enol also serves as an intermediate in the interconversion of the hydroxy ketones and the α-diketone, X. It is an energetic reducing agent which decolorizes indophenol dyes as readily as do the well-known cyclic di-enols ascorbic acid and reductone. In contact with air it is oxidized rapidly to hydrogen peroxide and the α-diketone. The diketone, in turn, when it is reduced catalytically, yields colorless solutions that are indistinguishable from those which are obtained by acidifying the magnesium derivative of the di-enol. Here, clearly the di-enol is formed by 1,4-addition to the diketone.

In solution this diketone slowly enolizes, forming an equilibrium mixture which in alcohol is composed of approximately equal quantities of ketone and enol. As the system

$$(C_6H_5)_2CHCOCOC_6H_2(CH_3)_3 \rightleftarrows$$

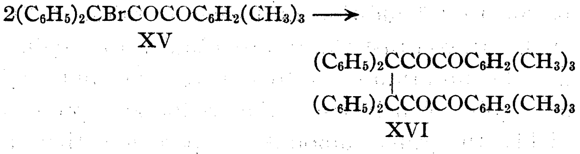
X (a)

$$(C_6H_5)_2C=C(OH)COC_6H_2(CH_3)_3$$

X (b)

is uncommonly sluggish both the ketonic and the enolic forms can be isolated without much difficulty.

The ketonic form is stable in the air, but like other α-diketones it is oxidized by alkaline hydrogen peroxide, the products being diphenyl acetic and mesitylene carbonic acids. It forms exceedingly reactive halogen compounds that lose the halogen when they are shaken with metals, leaving residues which couple to a highly phenylated tetraketone



$$2(C_6H_5)_2CBrCOCOC_6H_2(CH_3)_3 \longrightarrow$$

XV

$$\begin{array}{l}(C_6H_5)_2CCOCOC_6H_2(CH_3)_3\\ \quad\quad\quad\;|\\ (C_6H_5)_2CCOCOC_6H_2(CH_3)_3\end{array}$$

XVI

The enolic form is comparatively stable in the solid state but in solution it is oxidized rapidly by free oxygen, being cleaved thereby to benzophenone and trimethylphenyl glyoxylic acid. It is also oxidized by such mild oxidizing agents as ferric chloride but the result is synthesis instead of cleavage, the product being the same tetraketone that is formed by the removal of bromine from the bromo ketone.

As a consequence of the sluggishness of the keto–enol system the diketone and its enol do not, as might be expected, give the same products when they are treated with Grignard reagents. Both substances liberate approximately one mole of gas from methylmagnesium iodide but while the ketone is reduced to the di-enolate XII, the enol is converted into a magnesium derivative which on acidification yields only β-phenyl benzalacetomesitylene. All attempts to establish the struc-

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(4) Madelung and Oberwegner, *Ann.*, **490**, 201 (1931).

ture of this magnesium derivative were unsuccessful but presumably it is an allenic compound

$$(C_6H_5)_2C{=}C(OH)COC_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2C{=}C{=}C(OMgX)C_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2C{=}CHCOC_6H_2(CH_3)_3$$

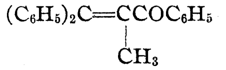
Having found that mesitylene derivatives can be employed for establishing the manner in which hydrogen adds to α-diketones, we undertook to utilize them also for ascertaining the mode of reduction of α,β-unsaturated ketones. To this end we reduced β-phenylbenzal acetomesitylene both catalytically and with zinc and acid. Some years ago Straus[5] inferred, from the nature of the products obtained from a series of unsaturated ketones, that in the catalytic reduction of these compounds 1,2- and 1,4-addition are competing reactions and that the outcome depends upon the same factors that control the mode of addition of Grignard reagents. Our experiments bring a measure of support to this inference. When phenylbenzal acetomesitylene was reduced with hydrogen and palladium on calcium carbonate the product was a mixture of approximately 88% of benzhydryl acetomesitylene and 12% of its enol. It is certain, therefore, that in this case at least 12% of the product is due to 1,4-addition of hydrogen but we were unable to determine whether the saturated ketone is due to 1,2-addition or to ketonization of the enol. In contrast the results obtained by reducing the unsaturated ketone with zinc and acid are quite conclusive; the reduction product yields the same amount of peroxide that is formed from the product obtained by adding phenylmagnesium bromide to benzalacetomesitylene. The reduction of α,β-unsaturated ketones with metal combinations, therefore, involves 1,4-addition to the conjugated system.

From the foregoing account it is evident that in every case in which it has been possible to establish the structure of a magnesium derivative resulting from the addition of a Grignard reagent to the conjugated system of an unsaturated ketone it has proved to be an enolate due to 1,4-addition. As the list now includes open chained and cyclic ketones, ketones with and without substituents in the α-position it is reasonable to assume a similar mode of addition to all systems of this type. It now seems clear, also, that the mode of alkylation and acylation of the enolates of mono ketones is associated in some manner with the stability of the corresponding enol, and it seems probable that the rate at which the enolic radical or ion is ketonized determines the relative amounts of C and O products that are formed.

Experimental Part

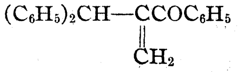
I. Alkylation

The two products obtained from each magnesium derivative were separable by crystallization. Facility of hydrolysis to the saturated ketones by acids was accepted as adequate proof of the O-alkyl derivatives. The formula of the C-alkyl derivative of benzhydryl acetophenone is based on the fact that the unsaturated ketone obtained by the indirect elimination of methyl alcohol is reducible to α-methyl-β,β-diphenyl propiophenone. For this unsaturated ketone, therefore, only two formulas are possible, namely



$(C_6H_5)_2C{=}C(CH_3)COC_6H_5$

and



$(C_6H_5)_2CH{-}C({=}CH_2)COC_6H_5$

As the substance reduces permanganate and forms a dibromide from which it is regenerated by potassium iodide the first of these formulas is excluded. And in the case of the mesitylene derivative the corresponding formula for the unsaturated ketone is excluded by the fact that it readily adds a mole of ethylmagnesium bromide.

Alkylation of Benzhydryl Acetophenone.—To an ethereal solution of phenylmagnesium bromide prepared from 2.5 g. of magnesium was added 10 g. of benzal acetophenone. The mixture was boiled for half an hour, treated with 8.5 g. of chloromethyl ether and boiled for two more hours. After cooling, the clear ethereal layer was decanted from the paste adhering to the walls of the vessel, treated with ammonia and ammonium chloride and distilled with steam. The distillate contained only diphenyl and benzyl methyl ether. The oily residue contained the acetal. By suitable treatment it was obtained as a solid which crystallized from methyl alcohol in plates and melted at 64–65°. The yield was 4.65 g. or 30%.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.6; H, 6.7. Found: C, 83.6; H, 6.8.

The paste, left after decanting the ethereal solution, contained the C-alkylation product II. It was likewise treated with ammonia–ammonium chloride. The ether was thus obtained as a solid which crystallized from methyl alcohol in prisms and melted at 131–132°. The yield was 11 g. or 70%.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.6; H, 6.7. Found: C, 83.3; H, 6.6.

α-Benzhydryl-β-bromo Propiophenone, V.—As the C-alkyl derivative was not affected by either dilute acids or bases it was heated in a sealed tube for ten hours with a large excess of 50% hydrobromic acid. The solid product

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[5] Straus and Grindel, *Ann.*, **439**, 276 (1924).

crystallized from alcohol in fine needles melting at 163°. The yield was 91%.

Anal. Calcd. for $C_{22}H_{19}OBr$: C, 69.7; H, 5.1. Found: C, 69.9; H, 5.2.

α-Benzhydrylvinyl Phenyl Ketone, VI.—The bromo compound was converted into the unsaturated ketone by dissolving it in boiling alcoholic potassium hydroxide. The ketone crystallized from alcohol in coarse needles melting at 115°.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.6; H, 6.1. Found: C, 88.9; H, 6.3.

Unlike vinyl phenyl ketone itself this benzhydryl derivative shows no tendency to polymerize or undergo autoxidation. It is, however, readily oxidized by permanganate and in the presence of platinum it is rapidly reduced to α-methyl-β,β-diphenyl propiophenone.

The dibromide of the ketone crystallized from alcohol in prisms melting at 105°. It lost its bromine and regenerated the unsaturated ketone when it was boiled with methyl alcoholic potassium iodide.

Anal. Calcd. for $C_{22}H_{18}OBr_2$: C, 57.6; H, 4.0. Found: C, 57.7; H, 4.1.

α-Methyl-β,β-diphenylvinyl Phenyl Ketone, $(C_6H_5)_2C{=}C(CH_3)COC_6H_5$.—This isomeric unsaturated ketone was obtained in small quantities when the C-alkyl derivative was boiled with concentrated sodium ethylate. It crystallized from alcohol in prisms melting at 114°. Unlike its isomer it does not reduce permanganate.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.6; H, 6.1. Found: C, 88.5; H, 6.1.

Alkylation of Benzhydryl Acetomesitylene.—A solution of the magnesium derivative was prepared by adding 5 g. of the ketone to ethyl magnesium bromide formed from 0.6 g. of magnesium in 100 cc. of ether and 50 cc. of benzene, and boiling for half an hour. To this solution was added 2 g. of chloromethyl ether. The mixture was boiled for two hours, then decomposed with ammonia and ammonium chloride. The ethereal layer, on evaporation, deposited a mixture which was separated by extraction with low-boiling petroleum ether. The extract deposited the acetal III. It crystallized from methyl alcohol in needles melting at 92°. The yield was 77–80%.

Anal. Calcd. for $C_{26}H_{28}O_2$: C, 83.0; H, 7.6. Found: C, 82.8; H, 7.4.

The residue left after extraction with petroleum ether was recrystallized from methyl alcohol. It separated in prisms melting at 155°. The yield of the ether IV was 18–20%.

Anal. Calcd. for $C_{26}H_{28}O_2$: C, 83.0; H, 7.6. Found: C, 83.2; H, 7.7.

α-Benzhydrylvinyl Mesityl Ketone, VII.—The ether was heated to 100° with 50% hydrobromic acid and boiled for one and one-half hours with methyl alcoholic potassium hydroxide. In both cases the product was the unsaturated ketone. The ketone crystallizes from methyl alcohol in prisms melting at 109–110°. The yield was 90%. Like the corresponding benzene derivative it combines with bromine and reduces permanganate.

Anal. Calcd. for $C_{25}H_{24}O$: C, 88.2; H, 7.1. Found: C, 87.9; H, 7.4.

II. Acylation

The magnesium enolate of benzhydryl acetomesitylene was obtained either by adding phenylmagnesium bromide to benzalacetomesitylene or by boiling the ethereal solutions of the saturated ketone itself with a slight excess of ethylmagnesium bromide. For the purpose of getting solutions of the enol the enolate was decomposed with iced acid in the presence of ether, the ether solution washed with ice-water and rapidly dried with sodium sulfate. A titration with bromine showed that a solution prepared in this manner contained 90–95% of enol.

The Peroxide, VIII.—For the purpose of preparing the peroxide the ethereal solution obtained by acidifying the enolate was diluted with three or four times its volume of petroleum ether and then washed with ice-water. A rapid current of oxygen was passed through the moist solution for several hours to complete the precipitation of peroxide which began in about an hour. The peroxide was purified by solution in ether and reprecipitation with petroleum ether. It crystallized in small needles melting, with decomposition, at 116–117°. The yield was 90%.

Reduction. α-Hydroxy-β,β-diphenylpropionyl Mesitylene, IX.—The peroxide was reduced both with hydrogen in the presence of platinum and by shaking it for several hours at the ordinary temperature with potassium iodide and glacial acetic acid. In both cases the product was the hydroxy ketone. The second method was found to be the more convenient. By recrystallization from hexane the hydroxy ketone was obtained in prisms melting at 76°. The yield was about 77%.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.7; H, 7.0. Found: C, 83.6; H, 7.1.

The acetate of the hydroxy ketone, prepared by acetylation with acetyl chloride, is convenient for identification because it is less soluble than the hydroxyl compound and crystallizes well from alcohol in prisms melting at 89°.

Anal. Calcd. for $C_{26}H_{26}O_3$: C, 80.8; H, 6.8. Found: C, 80.7; H, 7.0.

The benzoate, formed when the hydroxy ketone is treated with benzoyl chloride in pyridine, crystallizes from alcohol in prisms melting at 114–115°.

Anal. Calcd. for $C_{31}H_{28}O_3$: C, 83.0; H, 6.3. Found: C, 82.7; H, 6.5.

Isomerization, IX–XIV.—As the di-enol that is formed by adding excess of a Grignard reagent to the hydroxy ketone and acidifying the product, undergoes autoxidation much more rapidly than ketonization, the ordinary methods of manipulating organic magnesium derivatives yield only oxidation products. In order to secure a hydroxy ketone it was necessary, therefore, either to promote ketonization by addition of a base like piperidine or to prevent oxidation by addition of a reducing agent. The best results were obtained by the following procedure. An ethereal solution of 4 g. of the hydroxy ketone was added to a solution of ethylmagnesium bromide containing slightly more than two moles of reagent. The mixture was boiled for an hour then treated with excess of zinc dust and acidified by cautious addition of cold dilute acetic acid. The acidified solution was left to itself for a week in a securely corked flask before the product was isolated in the usual manner. The result was the isomeric hydroxy ketone. It crystallized from alcohol in prisms and melted at 77–78°. The yield was 90%.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.7; H, 7.0. Found: C, 83.6; H, 6.9.

The Dibenzoate, XI.—The hydroxy ketone was converted into a magnesium derivative as described in the preceding experiment, slightly more than two equivalents of benzoyl chloride was added to the resulting solution and the mixture was boiled for four hours. The result was a solid which crystallized from alcohol in prisms and melted at 157°. The yield was 80–85%.

Anal. Calcd. for $C_{38}H_{32}O_4$: C, 82.6; H, 5.8. Found: C, 82.4; H, 6.0.

The Diacetate.—As the compositions of the mono- and di-benzoates are too similar for differentiation by analysis, the diacetate was prepared in the same manner. It was obtained in two forms, the one melting at 127–128° and the other at 149°. Both forms crystallize well from alcohol.

Anal. Calcd. for $C_{28}H_{28}O_4$: C, 78.5; H, 6.6. Found: (128°) C, 78.4; H, 6.4. (149°) C, 78.7; H, 6.7.

Benzhydryl Trimethylphenyl Diketone, X.—When the solution, obtained by converting either of the isomeric α-hydroxy ketones into the magnesium derivative in the manner described in the preceding experiments and acidifying, is handled in the usual manner it absorbs oxygen from the air and the principal product is the α-diketone. In addition to the diketone there is formed a small quantity (3–4%) of a high-melting hydrocarbon (212°) which presumably is an indene derivative.

The diketone is obtained more readily, however, by oxidization of the α-hydroxy ketone. For this purpose a warm solution of the crude hydroxy ketone in glacial acetic acid is treated with a solution of slightly more than the calculated quantity of chromic acid in 95% acetic acid. The mixture is kept at 50° for half an hour, then poured into water. The diketone is extracted with ether and crystallized from alcohol. It separates in yellow cubes melting at 74–75°.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.2; H, 6.4. Found: C, 84.2; H, 6.7.

In the solid state the diketone appears to be completely stable. In solution it enolizes in part but in the absence of bases the process is exceedingly slow; the enolic form absorbs oxygen rapidly but no measurable quantity of oxygen was absorbed when an alcoholic solution of the diketone was shaken with oxygen for three and one-half hours. In the presence of a trace of piperidine or sodium methylate, however, it enolizes more rapidly and in the course of fifteen minutes forms an equilibrium mixture composed of nearly equal quantities of enol and ketone.[6]

Reduction of the Diketone.—When a yellow solution of the diketone in methyl alcohol was shaken with hydrogen and platinum it rapidly absorbed hydrogen and became colorless. A drop of piperidine was added to promote the ketonization and the solution was then set aside for thirty-six hours, before it was filtered and concentrated. The product was the higher-melting hydroxy ketone and the yield was 95%. The reduction was repeated, but the colorless solution was filtered immediately and the filtrate was allowed to evaporate in contact with air. It turned yellow and deposited the α-diketone in a yield of 95%. The solution which had been oxidized in the air also contained a considerable quantity of hydrogen peroxide. As the hydroxy ketone is insensitive to oxygen, the formation of the diketone is proof that the reduction product is the di-enol.

Reaction with Ethylmagnesium Bromide.—An ethereal solution of 3 g. of the diketone was added to a solution of ethylmagnesium bromide containing slightly more than two equivalents of the reagent. A small quantity of benzene was added to prevent precipitation of magnesium compounds, the mixture was boiled and then treated with acetyl chloride in slight excess. The product was the higher-melting diacetate of the di-enol—proving that organic magnesium compounds reduce the diketone to the magnesium derivative of the di-enol.

The Enolic Form of the Diketone, Xb.—The diketone was converted into the enol by dissolving it in a slight excess of 2% methyl alcoholic potassium hydroxide and pouring the red solution of the resulting enolate into excess of 2 *N* hydrochloric acid. It usually separated as an oil that soon solidified. The solid was washed with water and crystallized from methyl alcohol or low-boiling petroleum ether. It separated in pale yellow prisms melting at 117°. The yield was quantitative.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.2; H, 6.4. Found: C, 83.8; H, 6.6.

The Phenyl Urethan.—The enol can be identified by converting it into the phenyl urethan which is perfectly stable. It crystallizes well from ether and petroleum ether in pale yellow needles melting at 148°.

Anal. Calcd. for $C_{31}H_{27}O_3N$: C, 80.6; H, 5.9; N, 3.0. Found: C, 80.4; H, 6.2; N, 3.3.

Autoxidation.—In the absence of air the pure solid enol is fairly stable but all samples ultimately liquefy. Its solutions slowly absorb oxygen, the enol being oxidized to benzophenone, mesityl glyoxalic acid and mesitylene carbonic acid. When it is acylated it forms only O-acyl derivatives, the structure of the acylation products being definitely established by the fact that when they were reduced with zinc and acetic acid they formed the corresponding acyl derivatives of α-hydroxy benzhydryl acetomesitylene.

The acetate, formed by heating the enol with acetyl chloride on a steam-bath for ten hours, crystallized from petroleum ether in pale yellow prisms melting at 86–87°.

Anal. Calcd. for $C_{26}H_{24}O_3$: C, 81.2; H, 6.3. Found: C, 81.3; H, 6.4.

The benzoate, formed by benzoylation in pyridine, crystallizes from alcohol in pale yellow prisms melting at 124°. The yield was 90%.

Anal. Calcd. for $C_{31}H_{26}O_3$: C, 83.4; H, 5.9. Found: C, 83.3; H, 5.9.

Halogenation.—The halides that are formed by the addition of chlorine or bromine to the enol immediately lose halogen acid and form the halogen substitution products of the α-diketone. As the action of free chlorine involves

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(6) The statement of Kohler and Weiner [This Journal, 56, 434 (1934)] that benzhydryl phenyl diketone does not enolize is incorrect. A sample, equilibrated in methyl alcohol with a trace of piperidine, was titrated with bromine by H. E. Schroeder who found 15.5% enol.

substitution in the mesitylene group, the pure chloro compound is most readily made by employing a calculated quantity of sulfuryl chloride. The pure bromo compound can be made by operating with free bromine in chloroform at low temperatures. These halogen compounds are interesting because they are as reactive as the halogen derivatives of triaryl methanes. The constants of the chloro and bromo compounds as well as those of the corresponding ethers are shown in the following table.

	Calcd.		Found			M. p.,
	C	H	C	H	Form	°C.
$C_{24}H_{21}O_2 \cdot Cl$	76.5	5.6	76.4	5.9	Yellow plates	134
$C_{24}H_{21}O_2 \cdot Br$	68.4	5.0	68.1	5.4	Yellow plates	152
$C_{24}H_{21}O_2 \cdot OC_2H_5$	80.8	6.8	80.8	7.1	Prisms	121
$C_{24}H_{21}O_2 \cdot OCH_3$	80.6	6.5	80.6	6.8	Prisms	68

Coupling. The Tetraketone, XVI.—The enolic form of the α-diketone develops a brown color in alcoholic solutions of ferric chloride but the color soon fades. When the reaction was carried out with larger quantities the product was a sparingly soluble compound which crystallized from ether–petroleum ether in deep yellow prisms and which melted at 194°. The structure of this product was established by a synthesis from the bromo compound of the diketone. For this purpose a solution of 3 g. of the bromo compound in 50 cc. of dry benzene was shaken for twelve hours with 20 g. of mercury. The result was the same compound that had been obtained from the enol. The yield was 80–85%.

Anal. Calcd. for $C_{48}H_{42}O_4$: C, 84.4; H, 6.2; mol. wt., 682. Found: C, 84.1; H, 6.6; mol. wt., 685.

Catalytic Reduction of β-Phenylbenzal Acetomesitylene.—Preliminary experiments showed that the unsaturated ketone is reduced more rapidly by palladium on calcium carbonate than by platinum and hydrogen. Accordingly solutions of 4 g. of the ketone in ethyl acetate and in ether were shaken with hydrogen in the presence of 2 g. of the palladium catalyst until the calculated volume of hydrogen had been absorbed. The rate was the same in both solvents, the time required being an hour and three quarters. The suspensions were filtered, the filtrate was diluted with five times its volume of petroleum ether and saturated with oxygen. As the principal product was the saturated ketone, it was impossible to isolate pure peroxide but a crude estimate based on oxidation of acidified potassium iodide and on conversion to the enol of the diketone indicated that the mixture contained 10–12% of peroxide.

Reduction with Zinc and Acetic Acid.—A solution of 3 g. of the unsaturated ketone in 20 cc. of glacial acetic acid, 20 cc. of ether and 0.5 cc. of water was cooled in a freezing mixture and treated in the course of three minutes with 2.5 g. of zinc dust. The mixture was shaken in the freezing mixture for another three minutes, then poured in a mixture of 10 cc. of ether and 40 cc. of petroleum ether and washed rapidly with ice water until free from zinc and from most of the acetic acid. From the resulting ether–petroleum ether solution oxygen precipitated 3 g. of peroxide—a yield of 90%.

Summary

The paper presents evidence that the system $C{=}C(OH)C_6H_2(CH_3)_3$ is unusually persistent in solution. By utilizing this peculiarity it was possible to prove that the catalytic reduction of α-diketones proceeds by 1,4-addition to the oxygen atoms, that the reduction of α,β-unsaturated ketones with palladium on calcium carbonate and hydrogen proceeds at least in part by 1,4-addition to the conjugated system and that the reduction of α,β-unsaturated ketones by zinc and acid proceeds wholly by 1,4-addition.

CAMBRIDGE, MASS. RECEIVED MARCH 22, 1937

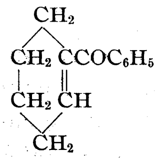
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

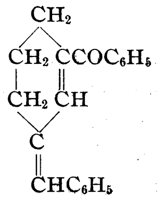
The Application of the Principle of Vinylogy to Unsaturated Ketones

BY R. E. CHRIST[1] AND REYNOLD C. FUSON

A methyl group, separated from a carbonyl group by one vinylene unit, exhibits properties that are similar to those which it possesses when it is attached directly to the carbonyl group.[2] The present paper is an extension of this principle to ketones in which the vinylene group forms a part of a six-membered ring.

Tetrahydrobenzophenone (I) was prepared from benzoyl chloride and cyclohexene by use of the Friedel–Crafts synthesis. This compound was of particular interest, inasmuch as it offered the possibility of testing whether the activating influence of a carbonyl group outside the ring could be exerted on a methylene group which was a member of the ring. The ketone was found to react with benzaldehyde in an alcoholic solution, sodium ethoxide being used as a condensing agent. The product isolated was the expected ketone (II).


I


II

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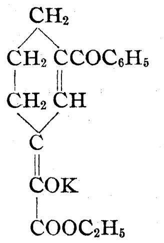
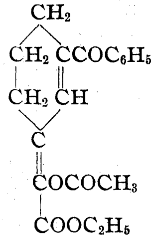
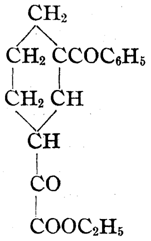
[1] Du Pont Post-doctorate Fellow.

[2] Fuson, Christ and Whitman, THIS JOURNAL, **58**, 2450 (1936).

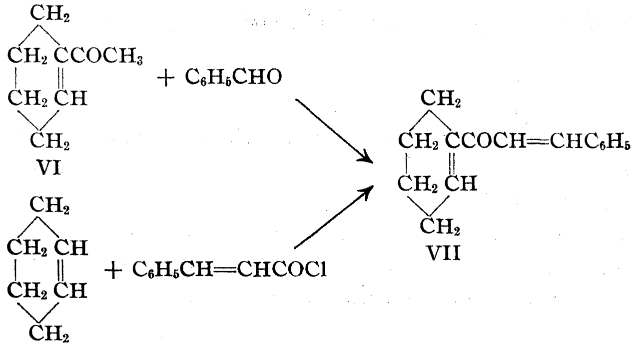
Tetrahydrobenzophenone was also condensed with ethyl oxalate in ether solution, potassium ethoxide being employed as a catalyst. The reaction led to the formation of the potassium salt (III). When treated with acetyl chloride, the salt was converted into the acetate (IV). The free keto ester (V) was produced by dissolving the potassium salt in water and acidifying with dilute hydrochloric acid.


III

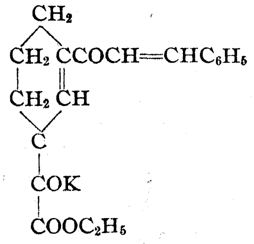

IV

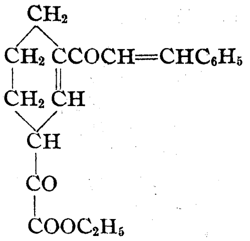

V

Tetrahydroacetophenone (VI) was chosen as a compound suitable for determining the relative reactivity of a methyl group adjacent to the carbonyl group and that of a methylene group separated from the carbonyl group by a linkage of the type —C=C—. The ketone was condensed with benzaldehyde in an alcoholic solution, sodium ethoxide being employed as a catalyst. The reaction product failed to give a positive iodoform test. This, along with its analysis, indicated that one molecule of aldehyde condensed with the methyl group in preference to the methylene group in the ring, giving the unsaturated ketone (VII). The identity of this compound was proved by its preparation from cinnamyl chloride and cyclohexene by means of the Friedel–Crafts method.

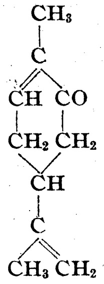


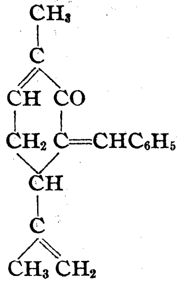
Benzaltetrahydroacetophenone (VII) in ether solution reacted with ethyl oxalate in the presence of potassium ethoxide to give the potassium salt (VIII). The free keto ester (IX) was produced by dissolving the salt in water and acidifying with dilute acid.

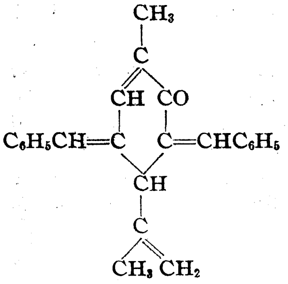

VIII


IX

Müller[3] reported that carvone (X) condensed readily with benzaldehyde in the presence of alkali to yield two different forms of benzylidenecarvone (XI). Wallach,[4] on the other hand, had reported the formation of an amorphous material.


X


XI


XII

The principle of vinylogy suggests the possibility of the formation of dibenzylidenecarvone (XII). For this reason, the reaction of carvone with benzaldehyde was restudied. The ketone and aldehyde were condensed in alcoholic solution, in the presence of sodium ethoxide, to give benzylidenecarvone. No attempt was made to separate the two forms. Instead, the mixture was condensed with benzaldehyde again, and a product was obtained whose composition was that of the expected dibenzylidenecarvone (XII). However, it could not be crystallized from ordinary solvents.

This is analogous to the condensation of one molecule of menthenone (XIII) with two mole-

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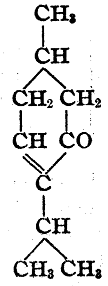
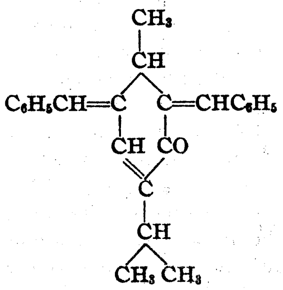
(3) Müller, *Ber.*, **54**, 1471 (1921).

(4) Wallach, *Ann.*, **305**, 274 (1899).

cules of benzaldehyde to produce dibenzylidenementhenone (XIV), as reported by Wallach.[5]



XIII



XIV

Experimental

Tetrahydrobenzophenone.—This substance was prepared by a modification of the method of Wieland and Beltog.[6]

One mole of benzoyl chloride, 86 g. of cyclohexene and 600 cc. of carbon disulfide were placed in a 2-liter, three-necked flask to which were attached a stirrer, reflux condenser and an inlet for aluminum chloride. The flask was cooled with an ice-bath and 133 g. of aluminum chloride was added cautiously while the solution was agitated vigorously. Afterward it was stirred for an additional six hours. The mixture was treated with iced hydrochloric acid, and the carbon disulfide layer was separated and dried with calcium chloride.

The solvent was removed, and 56 g. of potassium hydroxide, dissolved in 200 cc. of ethyl alcohol, was added. After three hours of refluxing, the alcohol was distilled. The residue was washed several times with water, and dissolved in ether. The solution was dried over calcium chloride and, after removal of the solvent, was distilled under reduced pressure. Two fractions were collected: (1) 74 g., b. p. 147° (8 mm.); n^{22}_{D} 1.5595; d^{22}_{4} 1.070; (2) 9 g., b. p. 174° (8 mm.).

Fraction (2) solidified upon cooling. Recrystallization from alcohol yielded colorless, well-developed needles melting at 110°. These were not studied further.

Fraction (1) was the desired tetrahydrobenzophenone, and represented a yield of 40% of the theoretical amount. It absorbed bromine readily, showing unsaturation.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: (semi-micro) C, 83.59; H, 7.75.

Condensation of Tetrahydrobenzophenone with Benzaldehyde.—To a solution of 6.2 g. of tetrahydrobenzophenone and 3.5 g. of benzaldehyde in 15 cc. of absolute alcohol maintained at 0° was added, with shaking, a solution of 1 g. of sodium in 10 cc. of absolute alcohol. The mixture soon assumed a gelatinous appearance, and gradually developed a reddish-brown color. It was allowed to stand for twelve hours in a stoppered flask. When it was diluted with water, a heavy yellow precipitate formed. Two crystallizations from alcohol gave faintly yellow crystals; m. p. 115°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: (semi-micro) C, 87.70; H, 6.67.

Condensation of Tetrahydrobenzophenone with Ethyl Oxalate.—A total of 7.8 g. of finely cut potassium was converted to potassium ethoxide by dissolving in 35 cc. of absolute alcohol. Two hundred cubic centimeters of dry ether was added, and the mixture was cooled to 0°.

To the ether solution was then added 18.6 g. of tetrahydrobenzophenone and 14.6 g. of ethyl oxalate dissolved in 50 cc. of ether. The mixture was allowed to stand for a period of twenty hours in an ice box; a heavy layer of orange crystals of the potassium salt (III) settled out.

The mixture was filtered rapidly, and the potassium salt was then washed several times with dry ether, and finally dried in a desiccator under reduced pressure. The weight of the final product was 29 g.; yield 89%.

The keto ester (V) was prepared by dissolving 19 g. of the potassium salt in 100 cc. of cold water and neutralizing with an excess of dilute hydrochloric acid solution. The ester was thrown out of solution as a yellow, semicrystalline mass. Two crystallizations from alcohol gave beautiful, faintly yellow needles. This compound begins to assume a deeper color at 85°, and finally melts at 92°. It dissolves in alkali, giving a light yellow solution.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.29; H, 6.34. Found: (semi-micro) C, 71.00; H, 6.32.

Reaction of the Potassium Salt (III) with Acetyl Chloride.—Ten grams of the salt was mixed with 5 g. of acetyl chloride dissolved in 75 cc. of ether and allowed to stand for a period of twenty hours at room temperature.

Water was added, and the insoluble ether layer was separated and washed several times. The solvent was then evaporated, leaving a yellow crystalline mass of the acetyl derivative (IV). Two crystallizations from alcohol gave 4.5 g. of almost colorless needles; m. p. 92°.

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.47; H, 6.14. Found: (semi-micro) C, 69.53; H, 6.36.

Preparation of Tetrahydroacetophenone.—This compound was made by a modification of the directions of Darzens.[7]

A mixture of 158 g. of acetyl chloride, 172 g. of cyclohexene and 1 liter of carbon disulfide was placed in a 3-liter, three-necked flask to which was attached a stirrer, reflux condenser and an inlet for aluminum chloride. The flask was cooled to 0°, and 266 g. of aluminum chloride was added, with stirring. Afterward, the mixture was stirred for two hours at room temperature. It was then treated with iced hydrochloric acid. The carbon disulfide layer was separated and dried with calcium chloride.

The solvent was removed, and the residue was distilled twice at reduced pressure from an excess of sodium carbonate to eliminate hydrogen chloride. The fraction, having a boiling point of 195–200°, was collected as the tetrahydroacetophenone. The yield was 155 g., or 62% of the theoretical amount.

The semicarbazone, a known compound,[7] melted at 220–221°.

Condensation of Tetrahydroacetophenone with Benzaldehyde.—A solution of 24.8 g. of tetrahydroacetophenone and 21.2 g. of benzaldehyde in 100 cc. of 95% alcohol was cooled to 0°. Two grams of sodium dissolved in 40 cc. of absolute alcohol was added slowly, with shaking. The solution assumed a reddish color and took on a gelatinous appearance. The mixture was allowed to stand in a stop-

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[5] Wallach, *Ann.*, **305**, 273 (1899).

[6] Wieland and Beltog, *Ber.*, **55**, 2246 (1922).

[7] Darzens, *Compt. rend.*, **150**, 707 (1910).

pered flask for four days. Steam was then led through to remove the alcohol, and the residual material was dissolved in ether. The solution was dried over calcium chloride and distilled under reduced pressure. A total of 1.7 g. of unchanged reactants was recovered.

In addition, there was obtained 16.6 g. of a light yellow oil having a boiling point of 160–165° (4 mm.). When allowed to stand in a refrigerator for a short time, it solidified. Crystallization from alcohol gave almost colorless crystals; m. p. 68°. This substance was benzaltetrahydroacetophenone; it absorbed bromine readily, showing unsaturation. It failed to give an iodoform reaction.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.85; H, 7.60. Found: (semi-micro) C, 84.62; H, 7.79.

Benzaltetrahydroacetophenone.—This compound was prepared for comparison from cinnamyl chloride and cyclohexene by means of the Friedel–Crafts method.

One hundred twenty grams of cinnamyl chloride and 59.5 g. of cyclohexene were dissolved in 100 cc. of carbon disulfide. The solution was added dropwise to a mixture of 106.5 g. of aluminum chloride and 400 cc. of carbon disulfide maintained at a temperature of 0°. Stirring was continued for an additional two hours at room temperature. The mixture was hydrolyzed with iced hydrochloric acid. The carbon disulfide layer was separated and dried with calcium chloride.

The solvent was removed, and the remainder was distilled at reduced pressure from an excess of sodium carbonate to remove hydrogen chloride. Two fractions were collected: (1) Four grams, b. p. 80–130° (4 mm.). This fraction was not studied further. (2) Fifty grams, b. p. 160–165° (4 mm.). This fraction solidified upon cooling. Crystallization from alcohol gave almost colorless crystals; m. p. 68°. A mixed melting point with the benzaltetrahydroacetophenone described previously showed no depression.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.85; H, 7.60. Found: (semi-micro) C, 84.69; H, 7.77.

Condensation of Benzaltetrahydroacetophenone with Ethyl Oxalate.—To a solution of 4.9 g. of potassium in 22 cc. of absolute alcohol was added 150 cc. of dry ether, and the mixture was cooled in an ice-bath. To the solution was added a solution of 13.2 g. of the ketone and 9.1 g. of ethyl oxalate in 50 cc. of ether. The mixture was allowed to stand for a period of twenty-four hours in an ice box; a heavy layer of brilliant red crystals of the potassium salt (VIII) settled out.

The mixture was filtered, washed several times with dry ether, and then dried under reduced pressure. The weight of the final product was 19.2 g.; yield, 88% of the theoretical amount.

The keto ester (IX) was prepared almost quantitatively by dissolving the salt in cold water and neutralizing with dilute hydrochloric acid. The ester was thrown out of solution as a yellow, viscous mass. Two crystallizations from alcohol gave yellow crystals; m. p. 131–132°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.03; H, 6.46. Found: (semi-micro) C, 72.91; H, 6.58.

Condensation of Benzaldehyde with Carvone.—A solution of 75 g. of the ketone and 53 g. of the aldehyde in 200 cc. of absolute alcohol was cooled to 0°, and 10 g. of sodium dissolved in 75 cc. of absolute alcohol was added gradually, with shaking. The solution soon acquired a reddish-brown color and a gelatinous appearance. It was allowed to stand for an additional forty-eight hours at room temperature. The alcohol was removed by steam distillation, and the viscous residue was dissolved in ether. The solution was washed with dilute acid, dried over calcium chloride and then distilled under reduced pressure. There was recovered 15.3 g. of unchanged reactants. In addition, two other fractions were obtained:

(1) Forty grams, b. p. 153° (3 mm.), a faintly yellow color; $n^{24.5}D$ 1.6040. The analysis corresponded to benzylidenecarvone, which was found by Müller[3] to exist in two different forms. No attempt was made here to separate them, however, as the fraction was to be further treated with benzaldehyde to see if a dibenzylidenecarvone could be prepared.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.66; H, 7.62. Found: (semi-micro) C, 85.65; H, 7.64.

(2) Twenty-two grams of higher-boiling, yellow, viscous liquid whose range of boiling point varied from 180 to 225° at 3 mm. pressure. Most of the material distilled in the vicinity of 210° (3 mm.). When cooled, it formed a glassy solid which could be crushed to an amorphous powder. The properties were very similar to those of dibenzylidenecarvone described in the next paragraph.

Condensation of Benzylidenecarvone with Benzaldehyde.—To a solution of 20 g. of ketone, 9 g. of benzaldehyde and 50 cc. of absolute alcohol, cooled to 0°, was added slowly, with shaking, 2 g. of sodium dissolved in 25 cc. of alcohol. The solution changed to a brownish-red gelatinous mass after a short time. It was allowed to stand an additional forty-eight hours at room temperature, and was finally warmed for an hour on a steam-bath. The alcohol was then removed by steam distillation, and the residual viscous material was washed with dilute acid, extracted with ether, dried over calcium chloride and distilled under reduced pressure. Two fractions were obtained: (1) Two and five-tenths grams, having a b. p. of 153° (3 mm.). This was unchanged benzylidenecarvone.

(2) Fifteen and five-tenths grams, having a b. p. of 210° (3 mm.). This was a very viscous yellow liquid which, when cooled, formed a glassy solid that could be crushed to an amorphous powder, but which could not be crystallized from ordinary solvents. This was undoubtedly the amorphous material prepared by Wallach, but not analyzed or investigated further. The composition corresponds to dibenzylidenecarvone which would be the product formed by the condensation of two molecules of benzaldehyde with one of carvone.

Anal. Calcd. for $C_{24}H_{22}O$: C, 88.30; H, 6.80. Found: (semi-micro) C, 88.15; H, 6.94.

Summary

Tetrahydrobenzophenone (I) has been prepared from benzoyl chloride and cyclohexene by use of the Friedel–Crafts synthesis. The ketone was found to react with benzaldehyde and ethyl oxalate, due to the reactivity of hydrogen atoms on the γ-carbon atom.

Tetrahydroacetophenone (VI) has been pre-

pared in an analogous manner. It, likewise, was condensed with benzaldehyde, producing benzaltetrahydroacetophenone (VII), which, in turn, was condensed with ethyl oxalate to form the keto ester (IX).

Carvone (X) was condensed with two molecules of benzaldehyde to yield an amorphous product whose composition was that of dibenzylidenecarvone (XII).

URBANA, ILLINOIS RECEIVED MARCH 15, 1937

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

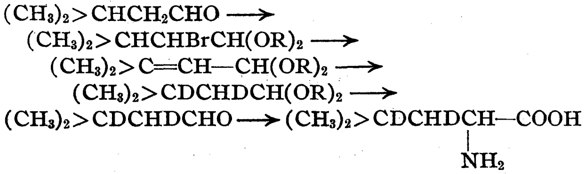
Dideuteriovaline and Dideuterioleucine

BY C. R. KINNEY AND ROGER ADAMS[1]

Analogs of two of the essential amino acids, valine and leucine, have been prepared in which two hydrogen atoms have been substituted by deuterium atoms. These new products are being tested in growth experiments to determine whether they may replace valine and leucine.

It is desirable, if not essential, for the deuterium to be introduced into such positions that during the reactions involved in the synthesis or in the animal body before metabolism actually starts, it will not be replaced by hydrogen. Thus, the deuterium atoms must not be substituted on the amino or carboxyl groups. Moreover, deuterium on a carbon atom from which rearrangement of the deuterium to oxygen or other similar atoms might take place, must be avoided.

The preparation of α-aminoisovaleric-β,γ-d_2 acid (dideuteriovaline) and of α-aminoisohexanoic-β,γ-d_2 acid (dideuterioleucine) from isobutyraldehyde and isovaleraldehyde, respectively, was carried out as illustrated by the following series of reactions for dideuterioleucine



$$\begin{array}{l} \mathrm{(CH_3)_2{>}CHCH_2CHO} \longrightarrow \\ \quad \mathrm{(CH_3)_2{>}CHCHBrCH(OR)_2} \longrightarrow \\ \qquad \mathrm{(CH_3)_2{>}C{=}CH{-}CH(OR)_2} \longrightarrow \\ \qquad\quad \mathrm{(CH_3)_2{>}CDCHDCH(OR)_2} \longrightarrow \\ \mathrm{(CH_3)_2{>}CDCHDCHO} \longrightarrow \mathrm{(CH_3)_2{>}CDCHD}\underset{\mathrm{NH_2}}{\underset{|}{\mathrm{C}}}\mathrm{H{-}COOH} \end{array}$$

It is obvious that in the intermediates isopentanal-β,γ-d_2 and isobutanal-β,γ-d_2, a deuterium on the carbon atom α to the aldehyde group exists; secondary in the former, tertiary in the latter. Both aldehydes theoretically are capable of enolization and thus it is possible that one of the deuterium atoms might be replaced at the intermediate aldehyde stage. A greater tendency to enolization would be expected in the molecule with the tertiary deuterium.

Analyses of the amino acids for deuterium indicated that the dideuteriovaline from the isobutanal-β,γ-d_2 contained about 25% less deuterium and the dideuterioleucine from the isopentanal-β,γ-d_2 6.5% less deuterium than the calculated amount. It is probable that an error of the magnitude of the latter might be introduced in the preparation of the isopentanal-β,γ-d_2 so that any appreciable loss of deuterium through enolization and hydrolysis is not indicated. On the other hand, the error of 25% in the dideuteriovaline probably is due in part to the purity of the isobutanal-β,γ-d_2, but principally to the replacement of deuterium by hydrogen during the transformation of the isobutanal-β,γ-d_2-diethylacetal through the aldehyde to the amino acid. In connection with these operations, it is significant that the deuterium in the intermediates, in spite of rather vigorous conditions in the presence of water and acids, is removed only where enolization may occur and then merely to a minor degree.

The authors desire to express their thanks to Dr. David Rittenberg of the Department of Biochemistry of Columbia University Medical School for his kindness in carrying out the deuterium analyses on the amino acids.

Experimental

α-Bromoisobutyraldehyde Diethylacetal.—Isobutyraldehyde was brominated according to the method[2] used for the preparation of α-bromoisovaleraldehyde diethylacetal. The crude product was fractionated carefully and the product, b. p. 78–82° (28 mm.), used for the subsequent reaction; yield 88%. Completely purified material boils at 80° (28 mm.).

Isobutanal Diethylacetal.—This was prepared according to directions[2] for making isovaleraldehyde diethylacetal except that it was found advantageous after treatment with molten potassium hydroxide to drop water slowly into the hot mixture until sufficient had been added to dissolve

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(1) For the last paper in this field see Leffler and Adams, THIS JOURNAL, 58, 1555 (1936).

(2) Fischer, Ertel and Loewenberg, *Ber.*, **64B**, 30 (1931); Dworak and Prodinger, *Monatsh.*, **53**, 590 (1929).

all the potassium bromide. The acetal was then separated, dried over solid potassium hydroxide and distilled; b. p. 136–139° (748 mm.); yield 71%.

Anal. Calcd. for $C_6H_{16}O_2$: C, 66.66; H, 11.11. Found: C, 66.52; H, 11.31.

Isobutanal-α,β-d_2 Diethylacetal.—Isobutenal diethylacetal was treated with pure deuterium as described in previous papers[1] using platinum oxide as a catalyst and ethyl acetate as a solvent. A large cell was employed so that the deuterium could be generated rapidly. The pure material which gave no permanganate reaction had a boiling point of 133–135° (747 mm.); d^{20}_{4} 0.8368; n^{20}_{D} 1.3938.

Anal. Calcd. for $C_8H_{16}D_2O_2$: C, 64.86; H + D, 12.31. Found: C, 64.60; H + D, 11.90.

Isobutanal Diethylacetal.—This was prepared by the reduction of the unsaturated acetal with hydrogen. It had the following constants: b. p. 135–136° (745 mm.); d^{20}_{4} 0.8295; n^{20}_{D} 1.3885. Oeconomides[3] reported the b. p., 134–136°; d^{12}_{4} 0.9957.

The calculated value for the density of isobutanal-α,β-d_2 diethylacetal on the assumption of the same molecular volume for deuterium and hydrogen[4] is 0.8408 as compared with the found value of 0.8368.

Dideuteriovaline (α-Aminoisovaleric-β,γ-d_2 Acid).—A mixture of 35 g. of isobutanal-α,β-d_2 diethylacetal (which did not react with potassium permanganate solution in three to four minutes), 125 cc. of water and 15 drops of concentrated sulfuric acid was stirred or shaken for thirty minutes. The reaction product was distilled slowly into a flask cooled in ice, containing 100 cc. of methanol and 35 g. each of ammonium chloride and potassium cyanide. When all of the aldehyde had distilled, the receiver was connected to a reflux condenser and refluxed for two hours. After cooling, 100 cc. of ether was added and the precipitated salt filtered and washed with ether. To the alcohol–ether solution 100 cc. of 40% aqueous hydrogen bromide and 25 cc. of water was added, and the mixture allowed to stand for two hours. It was heated under an air reflux until the alcohol and ether were removed. Some water was added to replace that lost by evaporation. The air reflux was replaced by a water-cooled one and the mixture refluxed for a total of twelve hours.

The solution was carefully evaporated to dryness, the final stages being carried out under reduced pressure. The solid was dissolved in about 200 cc. of water, the solution cooled in ice and well-washed silver oxide was added (from 50 g. of silver nitrate) in small lots. When an excess of silver oxide had been added, the solution was filtered and the precipitate well washed. Hydrogen sulfide was passed into the solution until no more silver sulfide precipitated. After filtering, the solution was evaporated until the amino acid began to crystallize out. Methyl alcohol was added and the solution cooled in ice; yield 12.2 g. (43.4%). The acid was recrystallized from water, using norite to remove a faint yellow color. If heated slowly, the melting point in a sealed tube was 273° with decomposition. The substance consistently melted 1.5–2° lower than pure *dl*-valine when both were melted in the same bath.

Anal. Calcd. for $C_5H_9D_2O_2N$: N, 11.76; D, 18.8 atom per cent. Found: N, 11.54, 11.44; D, 13.2 atom per cent. (±0.7).

Isopentanal-α,β-d_2 Diethylacetal.—Isopentenal diethylacetal was prepared[2] from isovaleraldehyde made from synthetic isoamyl alcohol. Difficulty was encountered in its reduction with deuterium. The best method was found to be by the use of dioxane (distilled from sodium) as a solvent, freshly distilled isopentenal acetal and Raney nickel as a catalyst. The product after fractionation gave a b. p., 164–165° (740 mm.); n^{20}_{D} 1.4025; d^{20}_{4} 0.8423.

Anal. Calcd. for $C_9H_{18}D_2O_2$: C, 66.66; H + D, 13.57. Found: C, 66.21; H + D, 12.59.

Isopentanal Diethylacetal.—This was prepared by reduction of the unsaturated acetal with hydrogen. It had the following constants: b. p. 167–168° (750 mm.); n^{20}_{D} 1.4040; d^{20}_{4} 0.8356. Alsberg[5] reported b. p. 168.2°; d^{12}_{4} 0.835.

The calculated value for the density of isopentanal-α,β-d_2 diethylacetal on the assumption of the same molecular volume for deuterium and hydrogen is 0.8464 as compared with the found value of 0.8423.

Dideuterioleucine (α-Aminoisohexanoic-β,γ-d_2 Acid).—The isopentanal-α,β-d_2 diethylacetal (which did not react with potassium permanganate solution in three to four minutes) was converted to dideuterioleucine following the procedure outlined for the valine derivative. The yield of acid recrystallized from water, using norite to remove color, was about 30% of the weight of the acetal. The melting point taken slowly in a sealed tube was 271° with decomposition. *dl*-Leucine in the same bath melted consistently 2° higher.

Anal. Calcd. for $C_6H_{11}D_2O_2N$: N, 10.52; D, 15.4 atom per cent. Found: N, 10.31; D, 13.7 atom per cent. (±0.7).

Summary

Dideuteriovaline (α-aminoisovaleric-β,γ-d_2 acid) and dideuterioleucine (α-aminoisohexanoic-β,γ-d_2 acid) have been prepared for comparison with valine and leucine in growth experiments.

Urbana, Illinois Received March 11, 1937

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(3) Oeconomides, *Bull. soc. chim.*, **35**, 500 (1881).

(4) McLean and Adams, This Journal, **58**, 804 (1936).

(5) Alsberg, *Jahresber. Fortschritte Chem.*, 485 (1864).

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

The Migration of Alkyl Radicals. I. Transfer of Some Tertiary Alkyl Radicals from Phenols to Hydrocarbons

BY RICHARD A. SMITH

In a study of alkyl phenyl ether rearrangement it was found that the migrating alkyl group can be introduced into a different molecule instead of merely rearranging to another part of the same molecule.[1] In this report the migration has been extended to apply to the change of position from the phenol nucleus to the benzene nucleus. As with the migration quoted, the reaction offers a means of preparation of alkylated benzenes. In some studies of rearrangements performed in this Laboratory by Niederl and the author, which have not been reported, it has been observed that alkyl groups in the phenolic ring can be made to change ring position under the influence of rearranging agents such as are used to effect phenyl ether isomerizations. It was thought that this migration might be intermolecular, in which case it should be possible to effect the migration to a foreign nucleus. Para substituted tertiary alkyl phenols were chosen as being very likely to undergo migration with the least possible side reactions. The action of aluminum chloride in the presence of benzene at room temperature and at reflux temperature upon *p*-*t*-butylphenol, *p*-*t*-amylphenol and 4-(1,1,3,3-tetramethobutyl)-phenol has been studied. The products are phenol and corresponding alkylbenzenes. With the butylphenol a good yield of *t*-butylbenzene was obtained; the reaction was carried out at the reflux temperature. The migration of the amylphenol was performed at room temperature. The migration of the octylphenol was performed at both room temperature and at the reflux temperature. There was no fundamental change in the reaction. The products identified were free phenol and *t*-butylbenzene. It will be noticed that the octyl group underwent scission. This is not unexpected as a Friedel–Crafts reaction between diisobutylene and benzene yields *t*-butyl substituted benzenes.[2] If this migration is bimolecular, the results may be interpreted as additional evidence for the para position of the octyl group in 4-(1,1,3,3-tetramethobutyl)-phenol.[3]

Procedure

I. The Action of Aluminum Chloride upon *p*-*t*-Butylphenol.—A half mole of the phenol, two-thirds of a mole of technical anhydrous aluminum chloride, and 150 cc. of benzene were refluxed for eight hours. The whole was then poured upon ice, the organic layer separated and water washed. The aqueous layers were extracted with ether, the ether layer dried with anhydrous sodium sulfate, the ether evaporated on a steam-bath, and the residual liquid purified by distillation and identified as phenol. The organic layer was washed with Claisen solution, water and then dried with anhydrous sodium sulfate. The product was purified by fractional distillation. A small Hempel column was found useful.

t-Butylbenzene, b. p. 167–168°; $n^{24}\text{D}$ 1.4958; d^{24} 0.868; yield 70%. *Anal.* Calcd. for $C_{10}H_{14}$: C, 89.6; H, 10.4. Found: C, 89.3; H, 10.1.

II. The Action of Aluminum Chloride upon *p*-*t*-Amylphenol.—A half molar quantity of the phenol and corresponding quantities of aluminum chloride and benzene as in (I) were allowed to stand at room temperature for twelve days. The whole was then worked up as in (I). Phenol was again obtained. The other product was purified by fractional distillation using appropriate sized columns.

t-Amylbenzene, b. p. 188–190°, $n^{24}\text{D}$ 1.5032; d^{24} 0.864; yield 25%.

III. The Action of Aluminum Chloride upon 4-(1,1,3,3-Tetramethobutyl)-phenol.—A six molar quantity of the phenol was treated with equivalent amounts of aluminum chloride and benzene at room temperature as in (II). A half molar quantity was treated at the reflux temperature as in (I). The products soluble in Claisen solution, in addition to phenol, are still under investigation.

t-Butylbenzene.—Yield in the cold (a) 50%; in the hot (b) 70%. Calcd. for $C_{10}H_{14}$: C, 89.6; H, 10.4. Found: (a) C, 89.9, 89.2; H, 10.4, 10.1.

The author wishes to acknowledge the help of Jack Rosen who performed a part of this work in connection with research for the degree of B.S. He wishes also to thank Miss R. T. Roth for the micro-analyses performed.

Summary

1. The migration of alkyl groups from a phenol nucleus to a benzene nucleus has been demonstrated.

2. The above migration has been performed

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[1] Smith, THIS JOURNAL, **56**, 714 (1934); also see Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933); Behaghel and Freiensehner, *Ber.*, **67**, 1368 (1934).

[2] Unpublished results of this Laboratory.

[3] Niederl, Smith and Whitman, THIS JOURNAL, **59**, 715–718 (1937).

at room temperature and at the reflux temperature.

3. The scission of the octyl group of 4-(1,1,3,3-tetramethobutyl)-phenol has been demonstrated.

4. *t*-Butylbenzene has been prepared from 4-*t*-butylphenol and from 4-(1,1,3,3-tetramethobutyl)-phenol. *t*-Amylbenzene has been prepared from 4-*t*-amylphenol.

5. Further studies of this type of migration are being made. Systems now under investigation include migrations from phenol nuclei of different types of alkyl groups to simple and substituted (phenol, phenyl ether and naphthol) aromatic nuclei.

NEW YORK, N. Y. RECEIVED JANUARY 19, 1935

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

Equilibria of the Reactions between Acetylene and Heavy Water at 0 and 100° and the Heats of Reaction[1]

BY L. H. REYERSON AND BRUCE GILLESPIE

In a previous communication[2] the equilibrium constants for the reactions between acetylene and heavy water at 25° were given. At equilibrium six different molecular species were involved in seven possible reactions and the constants for five of them were calculated from the experimental results. The experimental technique involved the accurate determination of the deuterium content of the heavy water before and after exchange. This investigation has been extended and the equilibria of the reactions have been determined at 0 and 100°.

The experimental methods with some small refinements remained much the same as in the previously reported study, except that a heavily insulated constant temperature air thermostat was substituted for the water-bath used in the earlier investigations. At 100° the normal alkaline solutions attacked the Pyrex glass bulbs so strongly that several of them broke during the time required for equilibrium. As a result quarter normal solutions of sodium hydroxide were used in the experiments run at 100° and half normal solutions were used at 0°. Because of the high partial pressure of water vapor at 100° the partial pressure of the acetylene was kept at about half an atmosphere to reduce the hazard of explosions. In all cases the bulbs containing the acetylene and heavy water solutions were made up and run at room temperature for several days, after which they were run at either 100 or 0° for from forty-eight to sixty hours. At the conclusion of a given run the heavy water was recovered from the bulbs and its density determined in the same manner as previously reported.[2] From the changes in the density of the heavy water solutions and a knowledge of the equilibrium constants K_6 for the reaction $D_2O + H_2O \rightleftharpoons 2HDO$ and K_7 for the reaction $C_2D_2 + C_2H_2 \rightleftharpoons 2C_2HD$ it was possible to calculate the number of moles of each of the six reacting molecules at equilibrium. According to Topley and Eyring[3] K_6 has a value of 3.118 at 0° and 3.374 at 100°. Glockler and Morrell[4] gave the value of K_7 at 0° as 1.373 and at 100° as 1.584. Tables I and II give the results of these calculations at 0 and 100°.

Using the values given in Tables I and II the equilibrium constants for the following exchange reactions were calculated.

$$C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O \quad (1)$$
$$C_2HD + HDO \rightleftharpoons C_2D_2 + H_2O \quad (2)$$
$$C_2H_2 + D_2O \rightleftharpoons C_2HD + HDO \quad (3)$$
$$C_2HD + D_2O \rightleftharpoons C_2D_2 + HDO \quad (4)$$
$$C_2H_2 + D_2O \rightleftharpoons C_2D_2 + H_2O \quad (5)$$

Table III gives the equilibrium constants for the exchanges at 0° and Table IV gives the values at 100°. The equilibrium constants at 100° are all higher than those previously reported at 25° and the values at 0° are all lower than at 25°.

It is of interest to note that Hiroto and Okamoto[5] calculated the equilibrium constant K_1 at 25° from spectroscopic data. They obtained a value of 0.59 where our experimentally determined value was 0.599. The agreement is excellent and

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(1) This investigation was made possible by a grant from the Graduate School of the University of Minnesota.

(2) L. H. Reyerson and Bruce Gillespie, THIS JOURNAL, 58, 282 (1936).

(3) Topley and Eyring, *J. Chem. Phys.*, **2**, 217–230 (1934).

(4) Glockler and Morrell, *ibid.*, **4**, 15 (1936).

(5) Hiroto and Okamoto, *Bull. Chem. Soc. Japan*, **11**, 349–351 (1936).

TABLE I

Initial percentage of D in water	Pressure C_2H_2, mm.	Moles of reactants in equilibrium at 0° H_2O	HDO	D_2O	C_2H_2	C_2HD	C_2D_2
99	642	0.009229	0.04323	0.06495	0.004426	0.01209	0.02407
99	354	.003929	.03116	.07928	.001141	.005049	.01628
44	730	.05883	.05179	.01462	.02805	.01348	.004715
44	366	.04989	.050095	.01613	.01254	.007486	.003255
25	610	.07624	.03379	.004803	.03045	.007745	.001435

TABLE II

Initial percentage of D in water	Pressure C_2H_2, mm.	Moles of reactants in equilibrium at 100° H_2O	HDO	D_2O	C_2H_2	C_2HD	C_2D_2
98	286	0.003154	0.02840	0.07580	0.0005849	0.003567	0.01374
55	310	.03420	.05131	.02282	.007337	.007325	.004616
28	374	.06554	.03671	.006095	.01556	.005981	.001452
28	322	.06443	.03725	.006382	.01331	.005125	.001246

TABLE III

Initial percentage of D in water	Pressure C_2H_2 mm.	Equilibrium constants at 0° K_1	K_2	K_3	K_4	K_5
99	642	0.583	0.425	1.819	1.325	0.773
99	354	.558	.406	1.740	1.267	.707
44	730	.546	.397	1.701	1.239	.676
44	366	.595	.433	1.854	1.350	.803
25	610	.574	.418	1.790	1.303	.748
Average		0.571	0.416	1.781	1.297	0.741

TABLE IV

Initial percentage of D in water	Pressure C_2H_2 mm.	Equilibrium constants at 100° K_1	K_2	K_3	K_4	K_5
98	286	0.677	0.428	2.286	1.443	0.977
55	310	.665	.419	2.245	1.417	.943
28	374	.685	.433	2.316	1.462	1.003
28	322	.666	.421	2.248	1.419	.946
Average		0.674	0.425	2.274	1.435	0.967

offers additional confirmation of the fact that equilibrium was reached by our method of investigation.

The values reported in Tables III and IV are given just as they came out in the calculation. No significance is attached to any figure beyond the second decimal place and it may not be correct. Taking the average value to two decimal places we have for the constants at 0° $K_1 = 0.57$, $K_2 = 0.42$, $K_3 = 1.78$, $K_4 = 1.30$ and $K_5 = 0.74$. At 100° the values would be $K_1 = 0.67$, $K_2 = 0.43$, $K_3 = 2.27$, $K_4 = 1.44$ and $K_5 = 0.97$.

Using these values together with those previously reported[2] it is possible to determine the heats of reaction for these isotopic exchanges. From the well-known equation of van't Hoff it is evident that the heats of reaction, ΔH, may be determined by plotting $-R \ln K$ (equilibrium constant) against $1/T$ (T in absolute temperature). The slopes of the curves so obtained give the values of ΔH. In Fig. 1 the values of log K are plotted against $1/T$. The resulting curves are practically straight lines. Using the slope of these curves and multiplying by -4.5787 to convert to $-R \ln K$ the values of ΔH in calories are obtained.

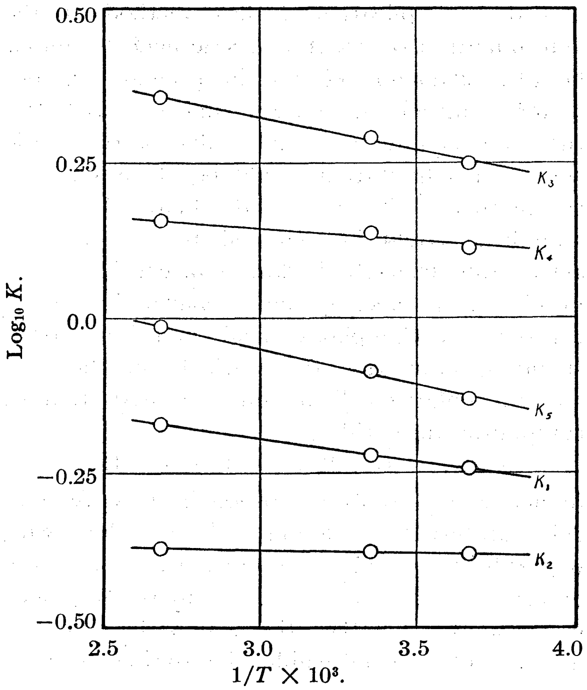

Fig. 1.—Variation of exchange equilibrium constants with temperature.

These values are given in Table V together with all of the equilibrium constants for the five reactions. As might well be expected the heats of reaction for these isotopic exchanges are very small.

TABLE V

Reactions	Equilibrium Constants 0°	25°	100°	ΔH
1	0.57	0.60	0.67	275
2	.42	.42	.43	35
3	1.78	1.95	2.27	480
4	1.30	1.37	1.44	175
5	0.74	0.82	0.97	530

Summary

1. The equilibrium constants for the reactions between H_2O, HDO, D_2O, C_2H_2, C_2HD and C_2D_2 have been determined experimentally at 0 and 100°.

2. From a knowledge of the change of the equilibrium constants of isotopic exchange reactions with the temperature (in the range 0 to 100°), the heats of reaction of these exchanges have been calculated.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 19, 1937

[CONTRIBUTION FROM THE LANKENAU HOSPITAL RESEARCH INSTITUTE]

A Polarimetric Method for the Determination of Water in Acetic Acid[1]

BY GERRIT TOENNIES AND MARGARET ELLIOTT

Some recently proposed methods for the determination of water in organic media are based on the acidimetric determination of acetic acid formed from acetyl chloride[2] or from acetic anhydride.[3] Application of these methods to the determination of water in acetic acid or similar liquids, although possible in principle, is obviously limited in accuracy and sensitivity by the large acidimetric blank value of the acetic acid. This limitation would be abolished if in the method of Toennies and Elliott[3] the acetic anhydride could be replaced by an optically active anhydride the hydration of which is measurable by an accompanying change in optical rotation. *d*-Camphoric acid and the corresponding anhydride differ widely in their effect on polarized light, but the hydration of camphoric anhydride

$$C_8H_{14}(CO)_2O + H_2O \longrightarrow C_8H_{14}(COOH)_2 \quad (1)$$

in acetic acid solution, although susceptible to acid catalysis,[4] was found to be too slow, with tolerably low acid concentrations (in presence of 0.1 M $HClO_4$ $k_{25} \cong 10^{-3}$), to be of practical promise. On the other hand, the complete absence of a conceivable[5] interfering reaction

$$C_8H_{14}(CO)_2O + 2CH_3COOH \longrightarrow C_8H_{14}(COOH)_2 + (CH_3CO)_2O \quad (2)$$

—in spite of the large excess of one of the potential reactants (CH_3COOH)—suggested the probability of a strong thermodynamic tendency for the opposite of reaction (2)

$$(CH_3CO)_2O + C_8H_{14}(COOH)_2 \longrightarrow 2CH_3COOH + C_8H_{14}(CO)_2O \quad (3)$$

This was found to exist: the bimolecular constant[6] of this reaction in acetic acid is directly proportional to the amount of strong acid present[7] and is, in the presence of 0.001 M perchloric acid and at about 25°, of the order of 10^{-1}; *i. e.*, with equal amounts of catalyst, reaction (3) is estimated to be 10^4 times as fast as reaction (1). Therefore, and since the acid-catalyzed reaction of acetic anhydride with moderate amounts of water in acetic acid is even more rapid than reaction (3), the following principle for the determination of water in glacial acetic acid suggests itself.

In the presence of a suitable small concentration of a strong acid (perchloric acid) the acetic acid solution of water is allowed to react with a measured quantity of acetic anhydride, and the unused amount of acetic anhydride is determined by the decrease in optical rotation coincident with its reaction with a measured amount of *d*-camphoric acid.

The experimental investigation of the method has been confined to a demonstration of its practicability and its minimum accuracy, while it has not been extended either to a quantitative study of various factors that might add to its refinement (such as temperature, concentration or mutual effects on the specific rotations of *d*-camphoric acid and *d*-camphoric anhydride) nor to a consideration of possible interfering substances (such as might conceivably be formic acid or

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[1] Aided by the Robert McNeil Fellowship maintained by McNeil Laboratories, Inc.

[2] D. M. Smith and W. M. D. Bryant, THIS JOURNAL, **57**, 841 (1935).

[3] G. Toennies and M. Elliott, *ibid.*, **57**, 2136 (1935).

[4] The catalysis of the hydration of organic anhydrides by strong acids in non-aqueous media, first suggested by observations of Orton and Jones [*J. Chem. Soc.*, **101**, 1708 (1912)] on acetic anhydride and confirmed by observations made in this Laboratory [Toennies and Lavine, *J. Biol. Chem.*, **100**, 474 (1933); Lavine and Toennies, *ibid.*, **101**, 732 (1933); ref. 3], has been studied by us on a number of anhydrides of different types, and widely differing rates of catalysis have been found (results to be published).

[5] The analogous reaction $(C_6H_5CO)_2O + 2CH_3COOH \longrightarrow 2C_6H_5COOH + (CH_3CO)_2O$ has been described: R. Kremann and W. Rösler, *Monatsh.*, **43**, 358 (1925); *C. A.*, **17**, 1426 (1923).

[6] All velocity constants are expressed in moles per liter per minute.

[7] G. Toennies and M. Elliott, abstracts of papers to be presented before the Division of Physical and Inorganic Chemistry at the Meeting of the American Chemical Society, Chapel Hill, N. C., April, 1937.

acetone[3]), nor to an exploration of its applicability to other acid or non-acid media.

Experimental

Reagents: Perchloric Acid Solution.—By dissolving a weighed amount of standardized concentrated perchloric acid in acetic acid[8] a solution of 1.00 *M* perchloric acid and 2.70 *M* water (exclusive of the water content of the acetic acid) was prepared. Repeated titration with an acetic acid solution of piperidine, with crystal violet as the indicator,[9] showed complete stability.

Acetic Anhydride.—The percentage of acetic anhydride (x) in a concentrated preparation was calculated from the average equivalent weight (e. w.) obtained by methylate titration[10,3] of a suitable aliquot dissolved in acetonitrile

$$\frac{x}{102.05} + \frac{100 - x}{60.03} = \frac{100}{\text{e. w.}}$$

The preparation used (Merck Reagent) showed 95.4 ± 0.2% acetic anhydride.

***d*-Camphoric Acid and *d*-Camphoric Anhydride.**—The camphoric acid used (Eastman) had a melting point of 187.5°, corr. (Beilstein 187°, corr.), and an equivalent weight, by methylate titration,[10,3] of 100.1 (calcd. 100.1). Determinations of the specific rotation[11] in acetic acid gave $[\alpha]_{\text{Hg}}^{27\pm1}$ + 53.9 ± 0.1° in 0.25 *M* solution, and $[\alpha]_{\text{Hg}}^{27\pm1}$ +54.25 ± 0.1° in 0.05 *M* solution, while *d*-camphoric anhydride in 0.25 *M* solution showed $[\alpha]_{\text{Hg}}$ −0.8 ± 0.2°. Ten cc. of acetic acid was found to dissolve at room temperature more than 0.5 but less than 0.6 g. of *d*-camphoric anhydride.

Reaction Velocities.—The velocity of the acid-catalyzed reaction between camphoric anhydride and water is illustrated by the experiment recorded in Table I. The bimolecular constant, calculated over the range of 25 to 89% conversion of the anhydride, shows a uniformly increasing trend which tends to disappear when it is assumed that the velocity is inversely proportional to the water content of the medium (Table I, column 4). This assumption may be justified as an approximation in view of the fact that H_2O, due to its basic properties in acetic acid,[12,9] will lower the acid potential of the catalyst

$$HClO_4 \begin{cases} +CH_3COOH \rightleftarrows CH_3COOH_2^+ + ClO_4^- \\ +H_2O \rightleftarrows H_3O^+ + ClO_4^- \end{cases}$$

In another experiment with initial concentrations in acetic acid, of 0.334 *M* H_2O, 0.550 *M* $(CH_3CO)_2O$, 0.219 *M* $C_8H_{14}(CO)_2O$ and 0.10 *M* $HClO_4$, the rotation (2-dm. tube, α_{Hg}) remained −0.03 ± 0.02° over a period of ten days, indicating that the water had reacted completely with the acetic anhydride and that reaction (2) does not take place. This, in conjunction with the following experiments showing the ease and completeness of the opposite reaction (3), seems sufficient evidence for the conclusion that under the experimental conditions a reaction between camphoric anhydride and acetic acid is thermodynamically impossible.

TABLE I

REACTION BETWEEN *d*-CAMPHORIC ANHYDRIDE AND WATER

Initial concentration of camphoric anhydride, b = 0.270 *M;* of water, estimated from water content of acetic acid, as determined (*v. infr.*), and from water introduced by 0.25 cc. of 10.9 *M* $HClO_4$, a = 0.362 *M*. Medium: acetic acid. Catalyst: 0.11 *M* $HClO_4$. Temperature: 24.0 ± 1.5°. $\alpha = \alpha_{\text{Hg}}$ measured in a 2-dm. tube. The values of the third column have been obtained by integrations over the successive intervals of time, and those of the fourth column by multiplying each value of the third with the mean value of the water concentration for each interval. In a control tube, without catalyst, (b = 0.273 *M*, a = 0.068 *M*) the rotation remained, over a period of seven days, α = −0.07 ± 0.02°.

Hours	α	$k \times 10^3$	$k(a - x) \times 10^3$
19.5	+1.41	0.75	2.47
43.5	+2.92	1.13	2.96
67.5	+3.99	1.59	3.21
90.0	+4.71	2.29	3.68
115.5	+5.20	2.73	3.63

The velocity of the reaction between camphoric acid and acetic anhydride (3) was investigated in the following experiments. A solution of the initial concentrations 0.067 *M* H_2O, 0.688 *M* $(CH_3CO)_2O$, 0.216 *M* $C_8H_{14}(COOH)_2$ and 0.001 *M* $HClO_4$ showed in the 2-dm. tube the following rotations:

Minutes	7	10	12	14	16	20	25	32
α_{Hg}	2.73°	2.22°	1.91°	1.60°	1.40°	0.90°	0.60°	0.32°

The temperature was 25–26°. Calculation of the bimolecular constants for the points of 20, 40, 60 and 80% conversion of the camphoric acid, obtained from the plotted curve and from the calculated initial and final rotations +4.67 and −0.06°, gives k = 0.135 ± 0.007, the assumption being made that the water present is eliminated at once by reacting with the equivalent amount of acetic anhydride. A similar solution containing 0.01 *M* perchloric acid showed after ten minutes the calculated value for camphoric anhydride. In the presence of 0.0001 *M* perchloric acid, on the other hand, the same reaction was 50% complete after twenty-five hours, while in the absence of any added catalyst a corresponding half time of ninety hours was found. No quantitative conclusions should be drawn from the latter two data, as without special precautions interference by contamination with minute amounts of either acid or basic material must be considered possible. However, on the basis of these experiments 1 to 5 × 10^{-3} *M* perchloric acid was selected as a catalytic agent suitable to ensure sufficiently rapid completion of the reaction of camphoric acid with acetic anhydride in the presence of an adequate excess of the latter.

Determination of Water Present in Glacial Acetic Acid.—The first experiment was based on the tentative assumption that the water content of the glacial acetic acid at hand ("assay 99.5% CH_3COOH") would be be-

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[8] Glacial Acetic Acid "Merck Reagent" was used throughout this work.

[9] J. B. Conant and T. H. Werner, THIS JOURNAL, **52**, 4436 (1930).

[10] T. F. Lavine and G. Toennies, *J. Biol. Chem.*, **101**, 727 (1933).

[11] For the polarimeter and light source used *cf. J. Biol. Chem.*, **89**, 155 (1930).

[12] N. F. Hall and J. B. Conant, THIS JOURNAL, **49**, 3055 (1927).

tween 0.3 and 0.7% (0.16–0.40 *M* water). An acetic acid solution containing 8.822 g. of 95.4% acetic anhydride (=8.5 cc.) per 100 cc. was used. To 6.44 mml. of camphoric acid in a 25-cc. flask 12.5 cc. of the acetic anhydride solution (10.31 mml. $(CH_3CO)_2O$) and 1.25 cc. of 0.1 *M* perchloric acid in acetic acid (=0.125 mml. $HClO_4$ with 0.34 mml. H_2O) were added, and the solution was completed to 25 cc. with acetic acid. The contribution of camphoric acid to the total volume under the conditions of these experiments was determined as approximately 0.845 cc. per gram. Accordingly the amount of acetic acid present is, with sufficient accuracy, 25.00−1.06 (acetic anhydride) − 1.09 (camphoric acid) = 22.85 cc. This solution showed after one hour a constant rotation of $\alpha_{Hg} = -0.08°$ (2-dm. tube), indicating complete conversion of camphoric acid into the anhydride. If the assumption is correct that acetic anhydride reacts much more rapidly with water than with camphoric acid this result shows that the acetic acid cannot have contained more than 10.31 (= total $(CH_3CO)_2O$) − 6.44 (= $C_8H_{14}(COOH)_2$) −0.34 (= H_2O introduced with $HClO_4$) = 3.53 mml. H_2O, *i. e.*, the water content was less than 3.53/22.85 = 0.154 *M* (0.278 g. per 100 cc.).

Accordingly the following two solutions were made, using the same stock solutions as in the preceding experiment: (A) 6.45 mml. $C_8H_{14}(COOH)_2$, 4.12 mml. $(CH_3CO)_2O$ and 0.12 mml. $HClO_4$ + 0.33 mml. H_2O and (B) 6.50 mml. $C_8H_{14}(COOH)_2$, 6.60 mml. $(CH_3CO)_2O$ and 0.125 mml. $HClO_4$ + 0.34 mml. H_2O, both completed to 25 cc. with acetic acid. After two hours the rotation (α_{Hg}, 2 dm.) was found to be stationary in both solutions, solution (A) showing +3.71 ± 0.005° and (B), +1.565 ± 0.015°. These values correspond to 33.0 and 71.2% conversion of camphoric acid into anhydride (obtained by using the values of +54.0 and −0.8° for the specific rotations of the two forms); *i. e.*, 2.13 and 4.63 mml. camphoric acid, respectively, have reacted with an equivalent amount of acetic anhydride. This leaves 4.12 − 2.13 = 1.99 and 6.60 − 4.63 = 1.97 mml. of acetic anhydride which must have reacted with equivalent amounts of water. 0.33 and 0.34 mml., respectively, are accounted for by the water introduced with the perchloric acid, leaving 1.66 and 1.63 mml. of water, which must have been present in the acetic acid. The amounts of the latter used were 25.00 − 1.09 (volume of camphoric acid) − 0.43 (volume of acetic anhydride) = 23.48 cc. and similarly 25.00 − 1.10 − 0.68 = 23.22 cc. so that 1.66/23.48 = 0.0707 *M* and 1.63/23.22 = 0.0702 *M* are the values obtained in two separate experiments for the water concentration, equal to 0.127 ± 0.0005% by volume.

Although the close agreement between the results of two determinations—in which the amounts (relative and absolute) of acetic anhydride used differed in the ratio of 5:8—seemed sufficient evidence for the validity of the method, this was verified by a set of determinations in which a known amount of water was added to the acetic acid. An additional purpose of this experiment was to see whether the time allowed for the reaction between acetic anhydride and water previous to the addition of camphoric acid could have any influence on the result, or, stated differently, if in the competition between camphoric acid and water for acetic anhydride the latter could be used up before all of the water had reacted. If this were possible the remaining water would react extremely slowly with camphoric anhydride (*cf.* under Reaction Velocities). 15.00 cc. of an acetic acid solution containing 52.16 mml. of $(CH_3CO)_2O$ (= 5.14 cc. 95.4% acetic anhydride), 0.520 cc. of H_2O (= 28.9 mml.) and 0.10 mml. of $HClO_4$ together with 0.27 mml. of H_2O were made up to approximately 100 cc. with acetic acid. The solution weighed 104.62 g. and contained the following amounts of water.

(100.00 − 5.14 − 0.52) 0.0705	= 6.65 mml.	(water content of the acetic acid, based on the preceding determination)
0.520/0.018	= 28.86 mml.	(added water)
	0.27 mml.	(introduced with $HClO_4$)
	35.78 mml.	

or 0.3420 mml. of H_2O per gram of solution.

25-cc. flasks, containing weighed amounts of camphoric acid, were filled to volume with the described solution, the exact amount of solution used being determined by weighing. Table II summarizes the results of this experiment.

TABLE II

DETERMINATION OF A KNOWN AMOUNT OF WATER IN ACETIC ACID SOLUTION

This table should be read in the light of the preceding text. The following notes, referring to the horizontal columns, will assist in its interpretation: $d = \frac{c \times 52.16}{104.62}$, $g = \frac{54.0 \times 2 \times e \times 0.2001}{f}$, $i = \frac{(g - h)100}{g + 0.075}$, $k = \frac{e \times i}{100}$, $l = d - k$, $m = l/c$.

(a)	Time between adding catalyst to the acetic anhydride-acetic acid–water mixture and combining the resulting solution (b) with camphoric acid, min.	6	12	120
(c)	Amount of solution (b) used, g.	24.97	24.79	24.95
(d)	Amount of acetic anhydride present, mml.	12.45	12.36	12.44
(e)	Amount of camphoric acid, mml.	6.50	6.72	6.49
(f)	Volume, cc.	25.05	25.00	25.10
(g)	Calculated initial rotation (2-dm. tube), α_{Hg}	5.61°	5.805°	5.59°
(h)	Final rotation, determined after 4 and 20 hours, α^{27}_{Hg}	2.265°	2.50°	2.285°
(i)	Fraction of camphoric acid converted into anhydride, according to (h), %	58.8	56.2	58.3
(k)	Acetic anhydride consumed by reaction with camphoric acid, mml.	3.815	3.775	3.78
(l)	Acetic anhydride consumed by reaction with water, mml.	8.635	8.585	8.66
(m)	Water initially present, per gram of solution (b), mml.	0.346	0.346	0.347

The amount of water found lies within approximately 1% of the calculated value and appears independent of the time allowed for the separate reaction between acetic anhydride and water, indicating that this reaction is much faster than the one between acetic anhydride and camphoric acid. This is in agreement with the data of Orton and Jones (*cf.* footnote 4) and is also evident from the observation, in this last experiment, of a considerable evolution of heat as soon as the catalyst was added even though its concentration was only 0.001 *M*.

Outline of a Practical Method.—The specific rotation of *d*-camphoric acid to be used is determined in about 0.25 *M* solution in glacial acetic acid. About 6.5 mml. of *d*-camphoric acid is weighed accurately in a 25-cc. volumetric flask, a definite amount of standardized acetic anhydride—the amount to be used is chosen so that after reaction with the expected amount of water 3.25 ± 3 mml. of $(CH_3CO)_2O$ remain for reaction with camphoric acid—is added and the flask is filled up to the mark with the acetic acid to be tested, including in the total volume 0.125 mml. of perchloric acid of known water content (*e. g.*, 0.125 cc. of a 1.00 *M* $HClO_4$ solution in acetic acid made from 70.0% aqueous perchloric acid would contain 0.299 mml. of H_2O). The amount of acetic acid employed is obtained by deducting the known volumes of the other ingredients from the total volume, using 0.845 as the partial specific volume of *d*-camphoric acid or, more accurately, by weighing. From the resulting solution a 2-dm. polarimeter tube is filled and polarimetric readings are taken until the optical rotation has become stationary. If the stationary value corresponds to the specific rotation of *d*-camphoric acid or to that of *d*-camphoric anhydride ($[\alpha]_{Hg} = -0.8°$) a new experiment with a larger or smaller amount, respectively, of acetic anhydride is started. The difference between the initial amount of acetic anhydride and the polarimetrically determined amount of camphoric anhydride formed is equivalent to the amount of water present. For confirmation of the result the determination should be repeated with a different amount of acetic anhydride.

Discussion

The amount of water present per gram of solution, expressed in the terms used in Table II, is

$$m = \frac{d}{c} - \frac{e(2 \times 0.2001 \times [\alpha]_1 \times e - fh)}{c(2 \times 0.2001 \times [\alpha]_1 \times e + 2 \times 0.1821 \times [\alpha]_2 \times e)}$$

where $[\alpha]_1$ and $[\alpha]_2$ are the specific rotations of camphoric acid and camphoric anhydride, respectively. By means of the probability theorems relating to the probable errors of arithmetically combined measurements,[13] the probable error of *m* may be calculated in algebraic terms. On the basis of the analytical experience of the present study the following estimated probable errors may be tentatively assigned:

Amount of acetic anhydride	d/c	±0.2%
Specific rotation of camphoric acid	$[\alpha]_1$	±0.3%
Specific rotation of camphoric anhydride	$[\alpha]_2$	±15%
Final rotation	h	±0.4%
Amount of camphoric acid	e/c	±0.2%

Application of these probable errors to the data results in a probable error, for the *single* determination, of ±1.8% in the most unfavorable case of determination *B* (p. 904 and of ±0.5% for each single determination of Table II. These computations, together with the actual results, point to a precision and probable accuracy of the method of at least ±1% for water concentrations of 0.1 to 1%. Undoubtedly this figure could be appreciably improved by more refined measurements.

A comparison of the analytical results with those obtainable by other methods has not been attempted as the limitations of available methods seemed to preclude the possibility of yielding results of comparable accuracy. Since the literature values[14] for the absolute freezing point of acetic acid vary at least between 16.62 and 16.67° an attempt to determine the freezing point of the acid used in the present work with an accuracy of 0.002°, corresponding to a variation in the water content of 0.001%, would appear futile. An alternative physical method based on critical solution temperatures,[15] although of about six times higher temperature sensitivity than the freezing point method, is also limited by the lack of absolute standard data. The chemical method of K. Fischer,[16] which is based on the fact that iodine is reduced by sulfur dioxide only in the presence of water, and which in regard to sensitivity is comparable with the present method, has not been applied by its author to acetic acid and may not be applicable without considerable additional research.

Summary

The amount of water present in acetic acid can be determined by allowing it to react with a known amount of acetic anhydride and by determining the excess of acetic anhydride by the decrease in optical rotation caused by its reaction with *d*-camphoric acid, by which the latter is converted into *d*-camphoric anhydride. Both reactions involved are strongly catalyzed by low concentrations of strong acids. The accuracy

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(13) *Cf. e. g.*, J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green & Co., New York, 1929, pp. 527–530.

(14) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Third Supplement, Verlag von Julius Springer, Berlin, 1936.

(15) D. C. Jones, *J. Chem. Soc.*, **123**, 1374 (1923).

(16) K. Fischer, *Z. angew. Chem.*, **48**, 394 (1935).

of the method is characterized by determinations of 0.1 and 0.6% of water, within limits of ±0.001 and ±0.008% respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Chemical and X-ray Investigation of Barium Sulfate Contaminated with Permanganic Acid[1]

BY PHILIP R. AVERELL AND GEORGE H. WALDEN, JR.

Introduction

A recent article by Walden and Cohen[2] reported the results of an investigation of barium sulfate precipitates contaminated with nitrate. The results of this work indicated the necessity of a similar investigation using a contaminating ion of different configuration, such as permanganate ion. Several investigators, notably Grimm and Wagner[3] have reported on the precipitation of barium sulfate in the presence of potassium permanganate.

The present investigation deals with (1) the precipitation of barium sulfate in the presence of permanganate ion, hydrogen ion being the only other foreign ion present; (2) the establishment, by chemical analysis, of the complete constitution of these contaminated precipitates, thereby identifying the cation which balances the charge of the coprecipitated permanganate ion; (3) investigation of the character of the precipitates by means of X-ray powder photographs.

It developed that the method of precipitation used by Walden and Cohen,[2] which for them produced beautifully coarse crystalline precipitates contaminated with nitrate ion, yielded for us precipitates so fine as to appear amorphous even when examined between crossed nicols under an oil-immersion objective, and which gave only a vague trace of an X-ray diffraction pattern. The method of precipitation used by Grimm and Wagner,[3b] adapted to the new conditions, proved to be apparently the only one which would yield precipitates of the desired coarseness.

Complete analyses of samples prepared by both methods showed that barium and sulfate ions exist in the precipitates always in a mole ratio of 1:1, which shows that the ion accompanying the permanganate ion is not barium, and therefore must be hydrogen or a hydrated hydrogen ion.

X-ray powder photographs showed a definite and fairly regular expansion of the lattice parameters with increased contamination, a conclusive evidence of the existence of solid solution.

Method of Preparation.—The method of precipitation used by Walden and Cohen, adapted to the study of permanganate contamination, consists of the slow addition of a sulfuric–permanganic acid solution to a barium permanganate–permanganic acid solution, the concentrations being so adjusted that the permanganate concentration is the same in both solutions; the sulfuric acid added is sufficient to precipitate less than half of the barium ion. The method of Grimm and Wagner, adapted to the present investigation, is to mix rapidly two solutions containing respectively equimolar quantities of barium permanganate and sulfuric acid. Each solution contains in addition permanganic acid in such amount that the permanganate ion concentrations are equal.

Since the unpreventable spontaneous decomposition of permanganic acid made it impossible to keep the system free of manganese dioxide, it was necessary to use all solutions as quickly after preparation as possible, and to use some means of removing manganese dioxide from the precipitate before final filtration, washing and drying. Accordingly, after the mother liquor was removed, the precipitate was given one washing with either sulfur dioxide solution or dilute hydrogen peroxide acidified slightly with hydrochloric acid, followed by water. All washings were made more effective by centrifugal drainage. As the slow drying of water-wet precipitates also caused decomposition with formation of manganese dioxide, this difficulty was obviated—again using Grimm's procedure—by washing with acetone four or five times, the last washings being colorless, then with anhydrous ether, before drying in air or over concentrated sulfuric acid.

The product thus prepared is a beautiful rose-colored precipitate, showing no traces of manganese dioxide, either to the unaided eye or under a microscope. As in the case of the precipitates described by Grimm, the co-precipitated permanganate ion is chemically very inert. The color is not noticeably bleached by contact with strong reducing solutions even after standing for several days. Heating at 110° for twenty to forty hours produces decomposition only in insufficiently washed precipitates, and in

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[1] Dissertation submitted by Philip R. Averell in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. The material was presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] Walden and Cohen, THIS JOURNAL, **57**, 2591 (1935).

[3] (a) Grimm, *Z. Elektrochem.*, **30**, 467 (1924); (b) Grimm and Wagner, *Z. physik. Chem.*, **132**, 131 (1928); (c) Wagner, *ibid.*, **2B**, 27 (1929).

those of highest contamination; in general, such heating causes not even a detectable loss in weight. One sample, after several hours ignition at 700–800°, showed the presence of undecomposed permanganate when dissolved in concentrated sulfuric acid.

Chemical Analysis

Two methods were used to decompose the barium sulfate precipitates for analysis: (1) fusion with anhydrous sodium carbonate; and (2) solution in concentrated sulfuric acid. In method (1), the melt was decomposed with a small amount of water, and a few drops of hydrogen peroxide added to reduce all the manganese to manganese dioxide. After filtration, the residue of barium carbonate and manganese dioxide was dissolved in dilute hydrochloric acid plus hydrogen peroxide; the barium was precipitated as the sulfate and weighed, while the manganese could be determined in the filtrate. The original filtrate, consisting of sodium sulfate and sodium carbonate, was made acid with hydrochloric acid, diluted to 400 cc., and the sulfate precipitated with barium chloride. In method (2), the coprecipitated permanganate was reduced to manganous ion by passing sulfur dioxide over the surface of the sulfuric acid during solution of the barium sulfate; the latter was then reprecipitated by adding water, washed, filtered, ignited and weighed; the filtrate was analyzed for manganese by the bismuthate method as modified and described by Park;[4] in place of potassium permanganate as a standard solution, ceric sulfate was used in conjunction with phenanthroline-ferrous ion indicator.[5] Samples of 0.5–1.5 g. required a titer of 5–10 cc. of 0.1 *N* ferrous sulfate; considering the accuracy of the bismuthate method, as well as the relatively small amount of permanganate ion in such a sample, these small titers yielded adequate precision in the calculations.

X-ray Analysis

Powder photographs were taken with the same apparatus used by Walden and Cohen[2] with a few mechanical improvements. The lattice parameters were calculated from film measurements by the least squares treatment developed by Cohen.[6]

Data and Interpretation

The equivalence of barium and sulfate ions in the precipitates was established by analyses of several precipitates by the sodium carbonate fusion method; representative precipitates prepared by both methods were analyzed. Table I shows the weights of barium sulfate obtained from the barium ion in the original precipitates (denoted by $\textit{Ba}\mathrm{SO}_4$ in the table, and from the sulfate ion (denoted by $\mathrm{Ba}\textit{SO}_4$). The upper group consists of precipitates in which the manganese dioxide was dissolved out with sulfur dioxide before the final washings with acetone and ether.

TABLE I

Ppt. no.	G. sample	G. $\textit{Ba}\mathrm{SO}_4$	G. $\mathrm{Ba}\textit{SO}_4$	Ratio Ba/SO$_4$
20	0.7486	0.6944	0.7056	0.984
22	1.0998	1.0429	1.0531	.990
24	0.9221	0.8798	0.8872	.992
42	.5545	.5357	.5418	.988
32	.9208	.8950	.8943	1.001
36	.8339	.7243	.7210	1.005
44	.5141	.4955	.4947	1.002
45	.3838	.3690	.3694	0.999
48	.5192	.4904	.4905	1.000

It will be noted that in these precipitates, the sulfate exceeds the barium by an amount distinctly outside the experimental error. Apparently washing with sulfur dioxide results in added contamination of the precipitate with excess sulfate ion formed on oxidation of the wash solution by manganese dioxide. When hydrogen peroxide solution was substituted for sulfur dioxide, this difference disappeared, as can be seen in the lower group, in which hydrogen peroxide was used to remove manganese dioxide.

As has been indicated above, the charge on the co-precipitated permanganate ion could conceivably be balanced in only three ways: (1) by barium ion, (2) by hydrogen ion or (3) by both barium and hydrogen ion. Since barium and sulfate ions are equivalent in the contaminated precipitates, alternatives (1) and (3) are thus ruled out; the permanganate ions must then be balanced wholly by equivalent hydrogen ions.

The demonstration of the equivalence of barium and sulfate also made it possible to use exclusively the sulfuric acid solution method of analysis, which actually measures only the barium content.

If the precipitates are considered to contain only barium sulfate plus permanganic acid, an appreciable portion of the weight of the original sample is left unaccounted for; that is, the weight of barium sulfate reprecipitated after solution in sulfuric acid, plus the weight of permanganic acid calculated from the manganese found by analysis, does not add up to the weight of sample used. The obvious explanation of this discrepancy is that the precipitates must contain water. Since permanganic acid is a strong acid, it would be present in the precipitating solution as oxonium and permanganate ions rather than anhydrous undissociated hydrogen permanganate molecules, and would be expected to enter the barium sulfate crystals in that form. As a matter of fact, our

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[4] Park, *Ind. Eng. Chem.*, **18**, 597 (1926).

[5] Walden, Hammett and Chapman, THIS JOURNAL, **55**, 2649 (1933).

[6] Cohen, *Rev. Sci. Instruments*, **6**, 68 (1935); Cohen, *Z. Krist.*, **A94**, 288 (1936).

analyses, so interpreted, indicate a variable proportion of water, but in only one instance does the determined ratio of moles of water to moles of permanganic acid fall below unity.

The composition of the contaminated precipitates may then be expressed as barium sulfate plus permanganic acid and water in varying proportions. Table II shows the numerical results of analyses of precipitates which were properly prepared, using hydrogen peroxide to clear up manganese dioxide, and which showed no traces of manganese dioxide. Precipitates in which sulfur dioxide was used are omitted.

Table II

Ppt. no.	$BaSO_4$, %	$HMnO_4$, %	% H_2O by diff.	Mole % hydrated $HMnO_4$
32	97.80	1.275	0.92	1.50
33	98.56	0.580	.86	1.13
34	90.25	6.601	3.15	12.5
36	86.53	9.027	4.44	16.9
42	97.08	1.844	1.08	3.57
44	97.57	1.448	0.98	2.81
45	97.48	1.521	1.00	2.95
46	98.54	1.417	0.04	2.72
47	96.20	2.174	1.63	4.21
48	95.43	2.542	2.03	4.93
49	98.18	1.178	0.64	2.28
50	96.26	2.269	1.47	4.39

Since the weight of water was calculated by difference, it was considered advisable to confirm the actual presence of water in the calculated proportion by some other method. Accordingly, weighed samples of different precipitates were given thirty minutes ignition at 700°. The ignited precipitates were weighed, then treated with 18 *M* sulfuric acid, the barium sulfate going into solution, and the residual manganese oxides remaining in suspension. After dilution with water to the proper volume, the barium sulfate being reprecipitated, a measured excess of standard ferrous sulfate solution was added and let stand until the manganese oxides were completely dissolved; the excess of ferrous sulfate was then titrated with standard ceric sulfate. Since the percentage of manganese in each sample was known already, and hence the weight of manganese present, the analysis after ignition yielded the average composition of the manganese oxides in the ignited precipitates. The observed weight loss during the ignition should then consist of the excess water, the water of constitution from permanganic acid, and oxygen from manganese heptoxide to the oxide of the determined average composition. From these data, the actual loss of water may be determined, and compared with the weight of water calculated by difference from the original analyses (see Table II). Since the oxygen and water of constitution of the permanganic acid amount to only a third of the total observed loss in weight, the remainder cannot be explained by experimental error. The only possible conclusion seems to be that the residual loss must be water, and this residual loss checks very well with the weight of water calculated by difference. The results are shown in Table III.

Table III

Ppt. no.	G. sample	H_2O by diff., g.	H_2O by ignition, g.
32a	1.1584	0.0096	0.0101
32b	1.1778	.0097	.0098
44	0.8989	.0088	.0083
47	.6363	.0077	.0073

This water is held tightly by the crystal lattice as shown by the fact that neither vacuum desiccation over concentrated sulfuric acid for four months, nor heating at 110° for a week caused any appreciable loss in weight. On the basis of this confirmation by a different method of attack, we may say with reasonable assurance that the precipitates definitely contain water.

In order to correlate our observations on permanganate contamination with those of Walden and Cohen on nitrate contamination, it was necessary to have complete analyses of their precipitates, which they had analyzed only for weight per cent. of nitrate ion. Two of the precipitates prepared by Walden and Cohen were selected and fused with anhydrous sodium carbonate to determine the ratio of barium to sulfate ion. As is shown in Table IV (nomenclature the same as in Table I), the difference between the barium and sulfate precipitates is in both cases about 6% of the sample weight, which is decidedly greater than any possible experimental error. However, the excess of barium does not account for the total nitrate content of the precipitates as given by the analyses of Walden and Cohen. Moreover, the remainder of the nitrate, when calculated to nitric acid, still does not account for the total sample weight, which indicates the

Table IV

Ppt. no.	G. sample	G. $\mathit{Ba}SO_4$	G. $Ba\mathit{SO}_4$	Ratio Ba/SO_4
12	0.6269	0.6072	0.5703	1.065
14	.4670	.4516	.4243	1.064

possibility that there may be water taken in as part of the contaminant. Although the data are too meager to warrant any definite statement as to the precise constitution of these precipitates, what does seem to be definite is that the ratio of barium to sulfate is greater than unity, and therefore that at least part of the co-precipitated nitrate has its charge balanced by excess barium ions. In this respect, the nitrate contaminated precipitates differ from those containing permanganate.

X-ray Data and Interpretation

The lattice parameters of the crystalline contaminated precipitates are given in graphical form in Figs. 1 and 2. In Fig. 1 the parameters a_0, b_0, and c_0 in Ångström units, and the volume of the unit cell, $a_0b_0c_0$, are plotted against weight per cent. of permanganic acid. In Fig. 2, the abscissa is the weight per cent. of total contaminant, or $100 - \%$ $BaSO_4$. The radii of the circles around the experimental points are the probable errors as determined by the least squares analysis of the films.[6] It is apparent from the two sets of curves that the lattice parameters vary more regularly with the percentage of total contaminant than with the percentage of permanganic acid alone. A reasonable interpretation of these results seems to be that the lattice is expanded by the entry of both permanganic acid and water, but not to the same degree. Since, as has been pointed out, the ratio of water to permanganic acid varies in different precipitates, it is not to be expected that the points will lie closely on a smooth curve, as should be the case if the expanding effects were the same, weight for weight. The fact that the lattice parameters vary with increasing percentage of contaminant demonstrates the solid solution character of the precipitates.

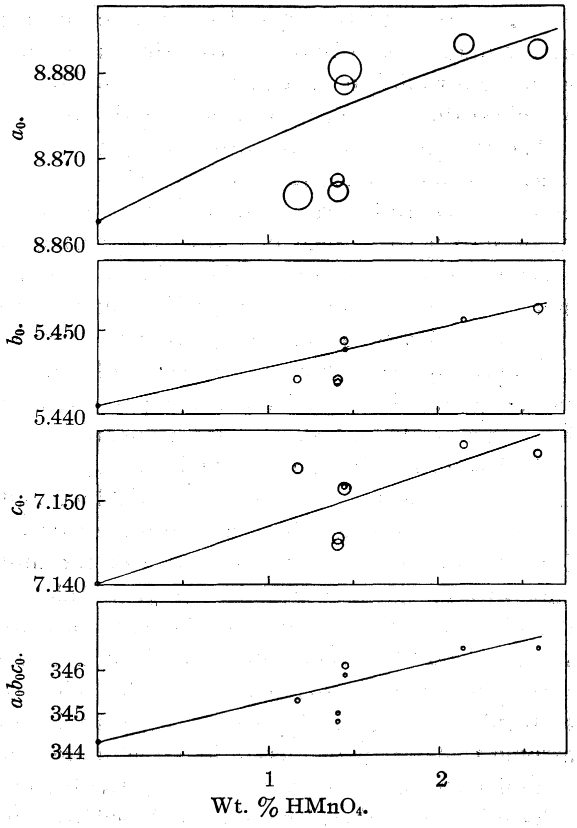

Fig. 1.

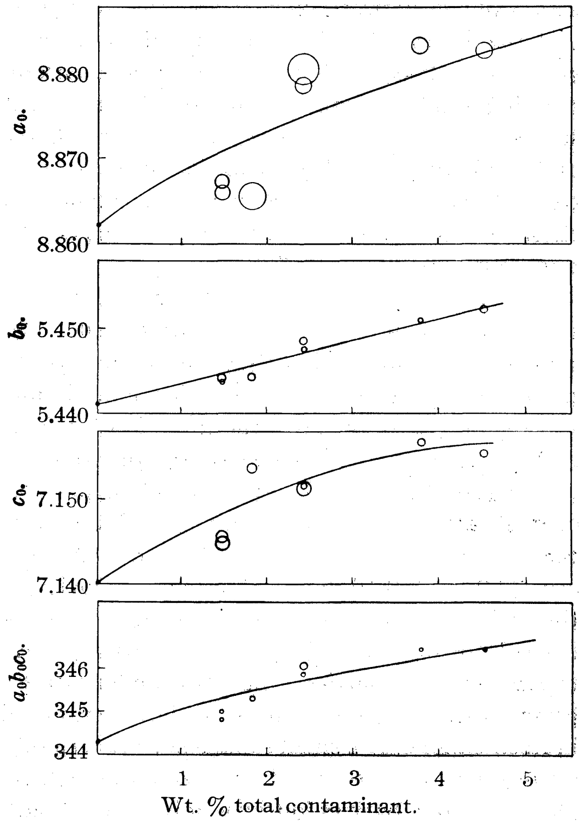

Fig. 2.

Discussion

It might be well at the outset to deal briefly with attacks[7] which have been made on the assumption of solid solution formation in precipitation systems on the ground that phase-rule studies of such systems show that no solid solution is found to exist in equilibrium with the mother liquor. It should be noted that there is no indication that any precipitate encountered in

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(7) Benrath and Schackmann, *Z. anorg. allgem. Chem.*, **218**, 139 (1934).

analytical practice involving coprecipitation of a foreign ion is in actual equilibrium with its mother liquor. Rather it has been observed that such equilibrium is approached exceedingly slowly during prolonged digestion.[8] Undoubtedly the precipitates investigated by the authors, as well as those of Grimm and Wagner and of Walden and Cohen, are not the results of heterogeneous equilibria, but of kinetic processes localized at the surfaces of the growing crystals.

The data just presented suggest that some of our present ideas with regard to the limitations under which solid solutions may be formed must be revised. The question of crystallographic isomorphism between solvent and solute appears to have as little bearing here as it does in metal systems.[9] Since large lattice expansions accompanying solid solution are not to be expected, it seems reasonable to suppose that the size, charge and configuration of the entering ions are controlling factors. The possible importance of these factors has already been discussed by numerous investigators.[3b,10]

This idea appears to be quite consistent with the experimental data just presented. The radius of a complex ion may be defined as the radius of the smallest sphere which can be circumscribed about the whole structure. Both sulfate and permanganate ions consist of four oxygens in regular tetrahedral arrangement about the central atom; the ionic radii, calculated from dimensions given by Wyckoff[11] and Pauling,[12] are 3.00 and 3.16 Å., respectively. Obviously the substitution of two permanganate ions for one sulfate ion could take place only with excessive expansion of the lattice. Substitution of a single permanganate ion for a sulfate ion, however, would in itself cause only a small expansion. Such a substitution would necessitate the simultaneous replacement of a barium ion by a univalent cation,[13] which would likewise cause no large expansion if there were a corresponding similarity of radii.

Although precise values of the radius of an oxonium ion are at present lacking, Volmer's[14] X-ray measurements of ammonium perchlorate and oxonium perchlorate (usually written $HClO_4 \cdot H_2O$) indicate rather definitely that oxonium ion is about the same size as ammonium ion, or slightly larger than barium or potassium ion. The ionic radii given by Wyckoff[11] are $NH_4^+ = 1.50$, $Ba^{++} = 1.38$ and $K^+ = 1.33$ Å. Peters[15] was able to prepare barium sulfate precipitates contaminated with as much as 12% of ammonium permanganate, and on the basis of his results predicted that oxonium permanganate should likewise form solid solutions in barium sulfate. Our experimental data fulfil this prediction. Whether the additional water molecules which the precipitates were found to contain are associated with the oxonium ions or are distributed elsewhere through the crystal cannot be decided by the data at our disposal. In either case, they would contribute to the expansion of the lattice, as indeed the experimental evidence indicates.

The nitrate ion has its three oxygens at the apices of an equilateral triangle, close-packed about the central nitrogen atom and planar with it, or nearly so. Since in nitrate-contaminated precipitates a barium ion is balanced by either one sulfate ion or two nitrate ions, it is necessary to have some idea as to what orientation two nitrate ions may assume with respect to each other in replacing a single ion. Such an idea may be obtained by a study of the lattice of barium nitrate.

Barium nitrate has a cubic lattice in which distinct pairs of nitrate ions lie symmetrically about alternate lattice points like the sulfurs in pyrites. The two nitrogens lie on a diagonal of the unit cube with the plane of both ions perpendicular to the diagonal; the oxygens of the two ions are staggered so that their projections on a plane perpendicular to the diagonal are at the apices of a regular hexagon. It seems permissible to assume that a pair of nitrate ions might present a similar configuration when entering the barium sulfate lattice in the place of a single sulfate ion. The radius of the nitrate pair in the barium nitrate lattice is 3.42 Å. These nitrate ions are not close-packed; if they were, the radius would be about 3.1 Å. There is no way to predict how closely the ions would pack if substitution occurred in this manner; however, either value is sufficiently close to the radius of a sulfate ion to suggest that such a substitution would cause no large expansion of the barium sulfate lattice.

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[8] Mellor, "Treatise on Quantitative Inorganic Analysis," 1st ed., Griffin, London, 1913, p. 614.

[9] Jette, *Am. Inst. Mining Met. Engrs., Inst. Metals Div., Tech. Pub.* 560 (1934); Hahn, "Applied Radiochemistry," Cornell University Press, Ithaca, New York, 1936, p. 69.

[10] Kolthoff and Moltzau, *Chem. Rev.*, **17**, 293 (1935).

[11] Wyckoff, "The Structure of Crystals," 2d edition, The Chemical Catalog Co., New York, 1931, p. 192.

[12] Pauling, THIS JOURNAL, **49**, 765 (1927).

[13] Huggins, *Chem. Rev.*, **10**, 427 (1932).

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

[15] Peters, Dissertation, Würzburg, 1930.

The correlation of these two cases of contamination involving different analytical results gives strong support to the assumption that size as well as charge and configuration of the ions concerned are very important factors controlling the formation of solid solutions in precipitation systems. The fact that, so far as is known, barium sulfate has only an orthorhombic form, while barium nitrate has only a cubic form, shows that for cases of partial miscibility isomorphism or structural similarity between any two component ion-pairs of the contaminated precipitate is immaterial to the process. Either cation or anion or both can be replaced independently.

Summary

1. Several samples of permanganate-contaminated barium sulfate were prepared in the absence of all foreign ions except permanganate and hydrogen ions, using the procedure employed by Grimm and Wagner.[3b]

2. Chemical analysis of the rose-colored precipitates shows that the total contaminant consists of hydrogen and permanganate ions in equivalent quantity, and a variable amount of water.

3. The lattice parameters of these precipitates, obtained by X-ray powder photographs, are all greater than those of pure barium sulfate, and when these are plotted against the weight per cent. of total contaminant present, a reasonably smooth, rising curve is obtained. The precipitates are, therefore, solid solutions.

4. Chemical analysis of nitrate-contaminated barium sulfate prepared by Walden and Cohen[2] shows that the mole ratio of barium to sulfate is greater than unity, and therefore that the coprecipitated nitrate ions are balanced, at least partially, by barium ions.

5. Comparison of permanganate contamination with nitrate contamination of barium sulfate shows that primary factors controlling the formation of solid solutions in precipitation systems are the size, charge and configuration of the ions entering the lattice. Crystallographic isomorphism and similarity of ionic structure are proved to be unnecessary conditions for cases of limited miscibility.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

The Vapor Pressure of Phosphorus Pentoxide

BY J. C. SOUTHARD AND R. A. NELSON

Introduction

The vapor pressure of phosphorus pentoxide has been subject to some uncertainty. The disagreement in existing data has already been pointed out by Kelley.[1] The uncertainty, however, is not so much one of magnitude as of reproducibility. Smits and co-workers[2] obtained measurements which varied from sample to sample. They believed this variation to be due to the presence of two forms of phosphorus pentoxide which could be partially separated by fractional distillation. It necessarily follows that these two postulated forms should be not readily transformable one into the other, and that true equilibrium between them could not have existed at the time the vapor pressure measurements were made. Entirely reproducible results were obtained by Hoeflake and Scheffer[3] but they point out that their distillations were carried out under fairly uniform conditions. Hence, their measurements were not necessarily at variance with those of Smits.

The present investigation was undertaken with the hope of determining definitely whether this phenomenon of Smits exists. The results are interpreted as showing that it does not and that the measurements of Hoeflake and Scheffer are substantially correct.

Description of Apparatus

The Jackson[4] type gage was used by both Smits and Hoeflake and Scheffer. It consists essentially of a thin-

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(1) K. K. Kelley, *Bur. Mines Bull.* 383, 1905, p. 82.

(2) A. Smits and A. J. Rutgers, *J. Chem. Soc.*, **125**, 2573 (1924); A. Smits with H. W. Deinum, *Z. physik. Chem.*, **A149**, 337 (1930). The same material is also presented in *Proc. Acad. Sci. Amsterdam*, **33**, 514 (1930).

(3) J. M. A. Hoeflake and F. E. C. Scheffer, *Rec. trav. chim.*, **45**, 191 (1926).

(4) Jackson, *J. Chem. Soc.*, **99**, 1066 (1911).

walled glass bulb collapsed on one side in such a manner that it is distorted easily by a difference in internal and external pressure. One end of the bulb is attached by a ring seal to an enveloping glass jacket and the other end to a long glass pointer. In practice the gage is used as a null instrument and the pressure in the external jacket is determined with a conventional mercury manometer. Hoeflake and Scheffer used such gages made of "fusible" glass, Jena glass and "verre dur"; Smits and Rutgers used gages made of high melting Jena glass and quartz while Smits and Deinum used quartz. The first measurements in this work were accordingly made with Jackson type gages constructed by Pyrex glass, Jena supremax glass and transparent silica glass (quartz).

The sensitivity of the gages used in this work was such that a difference in pressure between the inside bulb and the enveloping jacket of less than one millimeter of mercury could be detected. This was accomplished by observing the motion of the 35-cm. long glass pointer relative to a fine pointed tungsten reference needle through a ten-power reading telescope.

The pressure in the enveloping glass jacket was determined with an 8-mm. bore, two-meter long mercury manometer. The height of the mercury column was read with the unaided eye on a mirror backed scale which had been tested at the National Bureau of Standards. The readings were reduced to 0° and a gravity correction of 0.04 cm. per atmosphere ((980.091/980.665) × 76) applied.

The temperature of the gage was measured with a platinum–platinum–rhodium (10% rhodium) thermocouple. The noble metals of this couple were silver-soldered to copper wire and the junctions thus formed inserted in oil-filled glass protective tubes which in turn were immersed in a Dewar flask filled with crushed ice and distilled water. The e. m. f. developed by this couple was measured with a White potentiometer. Both the thermocouple and the potentiometer had been calibrated by the National Bureau of Standards.

Several furnaces were used, but all were provided with auxiliary heaters which permitted the temperature in the region surrounding the bulb to be maintained isothermal to ±0.2°, as shown by difference thermocouples located at various points.

At the higher temperatures these glass gages were attacked by the phosphorus pentoxide. In order to remove this objection and to escape errors which might have been inherent in the Jackson gage, it seemed advisable to make some measurements with an entirely different type of vapor pressure gage, preferably one which could be made of platinum and one which did not depend on diaphragm distortion. A gage which meets these requirements, but made of glass or quartz, has been used by Maier[5] in studying the vapor pressure of chlorides. This has been called the bulb type gage.

In this work it comprised a bulb of about 25-cc. volume connected by an approximately 30-cm. long, 1-mm. bore capillary to a glass U filled with mercury. The mercury in the capillary side of the U was kept at a reference mark by balancing an external pressure against it. In addition to the phosphorus pentoxide sample the bulb contained an inert gas (dry nitrogen) at a pressure of 15 to 20 cm. of mercury. This gas served as a means for transmitting the pressure in the bulb to the U-trap outside of the furnace, while such gaseous phosphorus pentoxide as diffused up the capillary was condensed on the walls. The pressure observed was thus approximately equal to the sum of the vapor pressure of the phosphorus pentoxide in the bulb and the pressure exerted by the inert gas. The latter was determined by extrapolation of pressure readings taken at temperatures where the vapor pressure was negligible. Three such gages were used, two made of Pyrex glass and one of platinum.

The disadvantages of this type of gage are due principally to the necessary presence of the inert gas. (1) Measurements are made with the substance under a pressure higher than its equilibrium vapor pressure. Under the conditions of these measurements the correction may possibly amount to as much as 0.1% but it has been neglected for lack of necessary data. (2) Equilibrium measurements are dependent on the rate of evaporation and diffusion of the substance in the bulb being faster than its rate of diffusion up and condensation in the capillary. (3) During vapor pressure measurements the pressure in the system is higher than during the simple inert gas pressure measurements. This results in an excess of inert gas in external or "obnoxious" volume of system over that prevailing during the blank measurements and in a corresponding decrease in the inert-gas pressure in the bulb. Correction for this is made as follows

$$P_{\text{corr.}} = (P_2 - P_1)(1 + (T_B V_A / T_A V_B))$$

where $P_{\text{corr.}}$ is the corrected vapor pressure, P_2 is the observed total pressure of inert gas and substance, P_1 is the pressure of inert gas and T_A, V_A, T_B, V_B the temperatures and volumes of the external and internal volumes, respectively. In our work this correction amounted to more than 2% at the higher temperatures.

The temperature–pressure measurements made and the furnaces used with the bulb type gages were the same as in the experiments with the Jackson type gages.

Measurements with the Jackson Type Gages

C. P. phosphorus pentoxide was distilled in a stream of oxygen at 800° in an iron tube furnace as described by Finch and Fraser.[6] This gave a product which showed a negative test for lower oxides with silver nitrate.[7] This distilled phosphorus pentoxide was loaded in a "dry box" into a tube which was immediately sealed onto a vacuum system comprising the vapor pressure gage with from one to three intermediate distillation bulbs, and the conventional trap, McLeod gage and mercury diffusion pump. After the system had been evacuated to less than 10^{-5} mm., the pentoxide was distilled first into the intermediate bulb or bulbs, and then into the gage. After the final distillation, the gage was sealed off and placed in the furnace after the system was shown to have no leaks.

The measurements obtained with the Pyrex glass gage are presented in Table I and Fig. 1. This gage without exception gave a reproducible zero position for the pointer on cooling down. Measurements in it on the vapor pressure of mercury gave results varying less than 0.2 cm. from the

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[5] C. G. Maier, U. S. Bureau of Mines Tech. Paper 360, 1925.

[6] G. I. Finch and R. R. Fraser, *J. Chem. Soc.*, 117 (1926).

[7] G. I. Finch and Peto, *ibid.*, **121**, 692 (1922).

values given in the "International Critical Tables." It was also subject to less attack by the phosphorus pentoxide than the gages made of either supremax or transparent silica glass. Readings were taken only when the temperature of the furnace was practically constant. As a rule check readings were made after a lapse of ten to fifteen minutes, and following a decrease as well as an increase in temperature. The data obtained with the Pyrex glass gage must accordingly be considered the most reliable of all those obtained by us with gages of the Jackson type. They differ but slightly from those obtained by Hoeflake and Scheffer. They show a metastable form (curve a, Fig. 1) existing below about 400°, a transient form (curve b, Fig. 1) and a stable form (curve c). The vapor pressure of the volatile form was entirely reproducible from day to day so long as the temperature did not exceed 360°. At 370° the rate of transition was such that satisfactory measurements could not be made. The transient form was considered by Hoeflake and Scheffer to be identical with that formed by supercooling the liquid. It could be obtained but once with the Pyrex gage. The curve c representing the stable form deviates from that of Hoeflake and Scheffer by an amount corresponding to about three degrees, which is not surely outside their limit of error. No satisfactory measurements on the vapor pressure of liquid phosphorus pentoxide could be obtained since the melting point lay above the workable range of a Pyrex gage.

TABLE I

VAPOR PRESSURE OF PHOSPHORUS PENTOXIDE IN PYREX GLASS JACKSON GAGE

t, °C.	$P_{\text{cm.}}$	t, °C.	$P_{\text{cm.}}$
Feb. 18, 1935		Feb. 20, 1935	
216.2	0.5	475.6	9.3
253.0	2.2	476.5	9.7
252.2	2.1	498.8	15.6
278.4	5.5	497.2	15.0
278.4	5.6	522.5	26.4
300.9	12.3	524.9	24.1
301.3	12.4	549.2	29.7
324.8	27.2	549.3	30.0
324.8	27.1	549.2	29.7
350.2	59.1	549.2	29.7
350.1	59.2	537.9	21.8
350.0	58.9	538.0	22.0
335.1	37.2	514.0	11.0
337.6	40.2	513.9	11.0
339.7	43.1	489.0	5.0
342.2	46.3	489.2	5.0
342.9	47.2	462.2	1.8
300.2	11.8	462.4	1.8
300.4	11.9		
		Feb. 21, 1935	
Feb. 19, 1935		449.3	1.4
283.6	6.6	474.1	3.4
283.7	6.6	474.1	3.3
316.5	20.7	474.2	3.4
316.1	20.6	498.4	7.1
316.0	20.5	498.0	7.1
336.6	39.6	525.1	15.1
337.2	40.2	525.1	15.2
337.7	41.1	561.7	40.9
358.7	76.0	562.1	41.3
360.7	79.1	562.8	42.2
360.9	79.6	562.9	42.4
361.2	80.2	534.3	19.9
361.3	80.3	534.3	20.1
362.3	82.1	534.3	20.1
362.7	82.3		
367.9	83.8	Feb. 25, 1935	
368.8	83.8	490.1	5.3
380.1	84.9	510.3	10.0
389.3	85.8	512.1	10.7

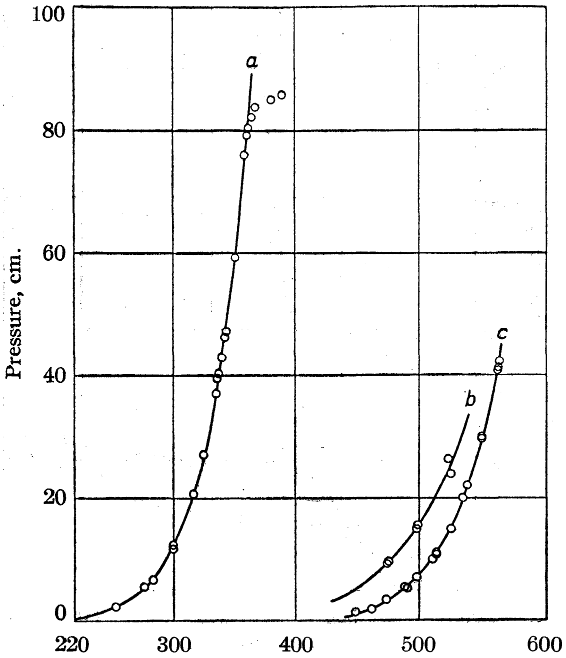

Fig. 1.—Vapor pressure of phosphorus pentoxide in Pyrex Jackson gage.

A gage was constructed from transparent quartz glass in an effort to obtain data on liquid phosphorus pentoxide. Also, it was thought desirable to duplicate Smits' working conditions as exactly as possible. Data obtained with this gage are given in Fig. 2. This gage showed a tendency for the position of the pointer to shift. At times this shift was equivalent to 5 cm. pressure. In most cases a suitable correction could be applied, but even then the measurements may be in doubt by more than a centimeter of mercury pressure.

The greatest fault of the quartz gage is the ease with which it is attacked by phosphorus pentoxide. Fairly reproducible measurements were obtainable at temperatures near 300°, but on maintaining the furnace at 350° overnight the pressure fell from about 50 to 18 cm. That this was not due to a transition to a more stable form is shown by the fact that a vapor pressure curve differing but slightly from the first measurements was obtained as soon as the temperature was lowered to a point where the gaseous phase was saturated. Furthermore, on three separate days (curves b, c, d, Fig. 2) measurements were obtained which were characteristic of a saturated vapor at the lower pressures and of a gas at the higher pressures. On each succeeding day not only was the temperature lower at which this break in the curve took place, but the pressure curves were lower. This could be explained by assuming that the phosphorus pentoxide was reacting with the walls of the gage. This assumption proved warranted as the gage was later found to be badly etched. In fact when the apparatus was inspected at the end of the series of runs, no phosphorus pentoxide at all was visible.

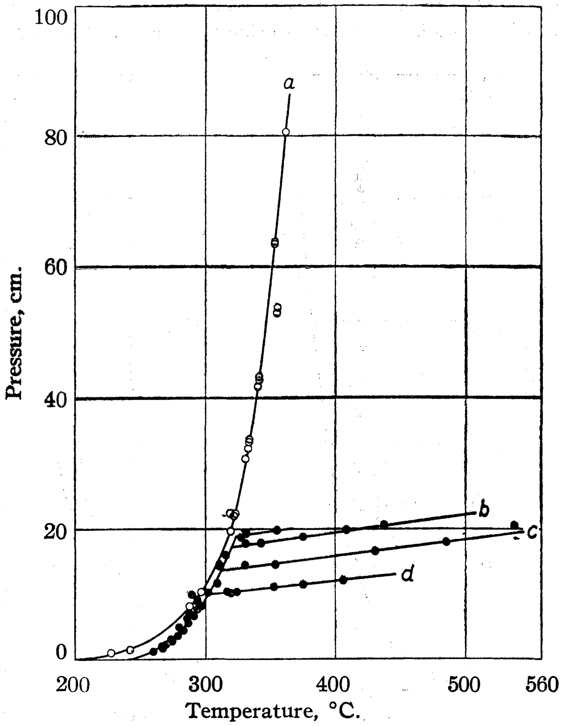

Fig. 2.—Vapor pressure of phosphorus pentoxide in transparent quartz Jackson gage.

Below 350°, however, some data were taken on the volatile form which do not differ by more than a centimeter or two from those obtained in the Pyrex glass gage. They were in general lower, as would be expected should contamination of the phosphorus pentoxide with silica have been occurring.

The Jena supremax glass gage was not entirely satisfactory either. In spite of its higher than Pyrex softening point its pointer was subject to some variation in zero position. The phosphorus pentoxide also finally disappeared into the glass walls although not so rapidly as in the quartz gage. The data obtained with this gage are shown in Fig. 3. No measurements could be obtained on the stable high temperature form. Curve b, Fig. 3, is almost identical with that of the amorphous form of Hoeflake and Scheffer. A reasonable explanation is that the phosphorus pentoxide suffered sufficient contamination by the supremax glass to prevent crystallization into the stable form.

Regardless of the glass used, the results obtained were not entirely above suspicion because some reaction with the walls occurred in all cases. This made measurements in a platinum system highly desirable.

Measurements with the Bulb Type Gage

Before building a gage from platinum, a series of measurements was made with the Pyrex bulb gages. This not only afforded an opportunity to study the reliability of the method, but offered an opportunity for comparing results obtained in the two types of gages made of the same material (Pyrex glass). There seems to be no systematic deviation between the observations obtained on the low temperature form with the two types. From necessity data on the bulb type gages had to be taken "on the fly" because if they were extended over too long a period the capillary tube would plug. The temperature of the furnace was consequently changing at a rate of about one to two degrees a minute during most readings. As a result the curves representing data taken during an increase in temperature will in general lie a degree or so higher than those representing the data taken during cooling. The mean, though, checks with the more static experiments of the Jackson gage.

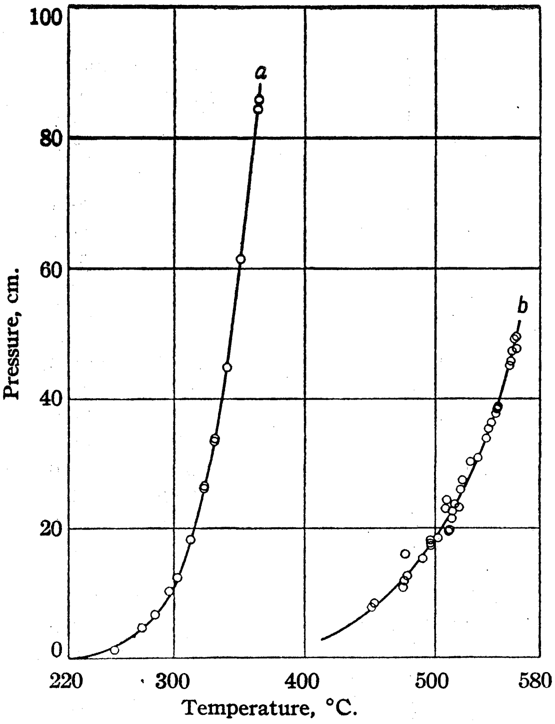

Fig. 3.—Vapor pressure of phosphorus pentoxide in supremax glass Jackson gage.

The platinum bulb gage presented a special problem in filling and sealing off, since dry phosphorus pentoxide cannot be handled in the open air. The upper end of the bulb was attached to a high vacuum system through the 30-cm. long platinum capillary tubes. The lower end of the bulb was provided with a short 1-mm. bore, gold lined, platinum capillary tube. To this was sealed a soft glass distillation apparatus which consisted of a bulb loaded with the pentoxide and but one intermediate bulb. The phosphorus pentoxide was first distilled under high vacuum into the intermediate bulb, the original container sealed off, and the phosphorus pentoxide finally distilled into the platinum bulb. These distillations were performed with the aid of an electrically heated tubular furnace at a temperature of about 300°. After the distillation, dry nitrogen was admitted to the system, the short platinum capillary was pinched shut and then sealed with gold. The bulb was then again evacuated to test for leaks and filled with dry nitrogen to a pressure of 15 to 20 cm.

The data obtained with the platinum bulb gage are presented in Fig. 4. They agree with the results obtained with the Pyrex Jackson gage on the two forms and in addition include five points which follow a curve assigned to the liquid phase by Hoeflake and Scheffer. The higher temperature measurements of August 20, 1936, obviously do not represent equilibrium since at one point the pressure rose from 90 to 110 cm. while holding the furnace temperature constant. This phenomenon took place in the course of about one hour. The possibility of such a pressure increase being due to a transition to another form having a higher vapor pressure is thermodynamically inconceivable. These data (of August 20) are included as being illustrative of the relative difficulty of obtaining equilibrium vapor pressure measurements on the high temperature form. Smits and Deinum (pp. 347, 348) experienced a similar difficulty and believed it to be due to lack of "internal equilibrium" between the postulated co-existent forms. If this had actually been the case it seems more reasonable that the pressure would have decreased rather than increased.

Results

The data obtained in this investigation together with those of previous workers are interpreted as showing that phosphorus pentoxide exists in two crystalline modifications. These are designated as the low temperature and high temperature forms, respectively.

The low temperature form has a vapor pressure which may be represented by equation (1)

$$\log_{10} p_{\text{cm.}} = -(5000/T) + 9.792 \qquad (1)$$

the high temperature form by equation (2)

$$\log_{10} p_{\text{cm.}} = -(7930/T) + 11.113 \qquad (2)$$

and the liquid by equation (3)

$$\log_{10} p_{\text{cm.}} = -(4320/T) + 6.809 \qquad (3)$$

Equation (1) gives 358.9° as the atmospheric sublimation temperature for the low temperature form. A temperature of 359.0° has been calculated from Hoeflake and Scheffer's[3] work by Frandsen.[8] Similarly the data of Smits and Deinum[2] give the three values 356.6, 362.0, 370.5° and the data of Smits and Rutgers 354.9 and 346.1°. The mean of these values based on the work of earlier investigators was thus estimated by Frandsen to be 358 ± 7°, which compares favorably with the value obtained here.

A solution of equations (2) and (3) determines the triple point between the liquid, high temperature solid form and gas as being at a pressure of 45.6 cm. and a temperature of 565.6°. The triple point pressure and temperature were found by Smits and Rutgers to be 0.59 atm. (44.8 cm.) and 563°; by Hoeflake and Scheffer to be 46 cm. and 569°; and by Smits and Deinum to be 55 cm. and 580°.

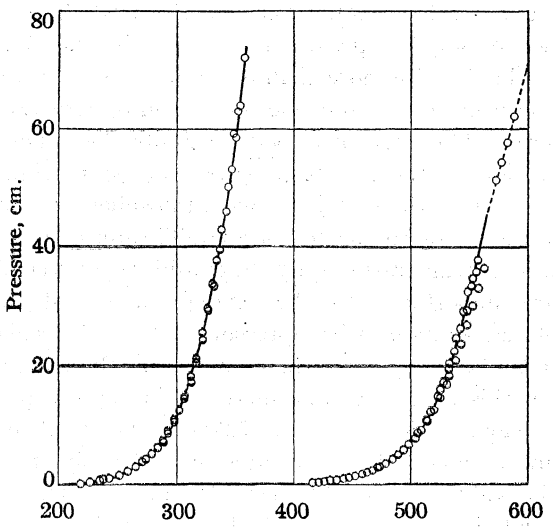

Fig. 4.—Vapor pressure of phosphorus pentoxide in platinum bulb gage: ———, vapor pressure of solid; - - - - - -, vapor pressure of liquid.

The heats of vaporization per gram molecule are determined from eq. (1) and (3) as 22,800, 36,200, 19,700 calories for the low temperature form, high temperature form and liquid, respectively. The heat of fusion is thus 16,500 cal. The only available calorimetric heat of vaporization work is that of Frandsen[8] on the low temperature form. He obtained the value 8800 ±1300 cal. per gram formula weight of phosphorus pentoxide.

To compare this calorimetric value with that calculated from the vapor pressure data it is necessary to have some knowledge of the molecular weight of the vapor. Vapor density determinations by West[9] at 1400° indicate a molecular weight of about 300, while measurements by Tilden and Barnett[10] at about 1000° range from 307 to 370. The molecular formula most nearly approaching these values is P_4O_{10} with a gram molecular weight of 284. The errors inherent in the vapor density determinations are such that they cannot definitely be said to disagree with this formula. However, the possibility

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(8) M. Frandsen, *Bur. Standards J. Research*, **10**, 54 (1933).

(9) C. A. West, *J. Chem. Soc.*, **81**, 923 (1902).

(10) Tilden and Barnett, *ibid.*, **69**, 154 (1896).

that the vapor is an equilibrium mixture of several forms must be considered. The composition of such a mixture would necessarily depend on the pressure, which in this case is the vapor pressure. Any wide variation in this composition would be reflected in the heat of vaporization, which would result in abnormal curvature of a log p *vs.* $1/T$ plot. The experimental data do not reasonably permit a variation in the slope of this line by more than a few per cent. between one atmosphere and one-tenth atmosphere pressure. This lack of curvature limits the concentration of the lowest polymer (P_8O_{20}) to something less than 5% at one atmosphere, if the variation of the association equilibrium constant in this temperature range be considered of secondary importance to the change of the degree of association with pressure. The molecular formula P_4O_{10} must therefore be nearly correct. On this basis the calorimetric value of the heat of vaporization becomes 17,600 ± 2,600 cal. per gram mole. This deviates considerably from the value 22,800 obtained here and 22,600 calculated from the data of Hoeflake and Scheffer.

Considerable importance is attached to the fact that phosphorus pentoxide vapor will condense only as the low temperature form. This indicates, at least, that the transition occurs only through the solid phase.

Acknowledgments.—The authors are indebted to P. H. Emmett, S. B. Hendricks, R. T. Milner and P. H. Royster for their advice and encouragement. Special mention should be made of the skillful glassblowing of Leonardo Testa in the construction of the Jackson type gages.

Summary

1. The vapor pressure of phosphorus pentoxide has been found to be entirely reproducible and independent of the rate of distillation of the sample.

2. The data are interpreted to show that phosphorus pentoxide exists in a low temperature and a high temperature crystalline form and as a liquid. The atmospheric sublimation temperature of the low temperature form was found to be 358.9°. The triple point between the high temperature crystalline form, the gas and the liquid was found to be at a pressure of 45.6 cm. of mercury and at a temperature of 565.6°. The rate of transition from the low to the high temperature form is undetectable below 360°.

WASHINGTON, D. C. RECEIVED FEBRUARY 23, 1937

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

Aging of Fresh Precipitates. XII. The Equilibrium between Mixed Crystals of Silver Chloride and Bromide and Solutions

BY H. C. YUTZY[1] AND I. M. KOLTHOFF

It is well known[2] that solid silver chloride and bromide form a complete series of mixed crystals. Küster,[3] preparing the mixed crystals by precipitation from solutions at 19°, was the first to study the equilibrium conditions existing between solid and solution. Various studies, more or less related to the subject, are found in the literature.[4–6] In connection with a study of the aging of precipitated silver chloride it was desirable to know the equilibrium conditions of distribution at 27 and 98°.

The relation between the distribution constant K and the composition of the liquid and the solid phase is found from the following considerations.

$$\mathrm{Cl}^- \text{ (crystal)} + \mathrm{Br}^- \text{ (solution)} \rightleftarrows \mathrm{Br}^- \text{ (crystal)} + \mathrm{Cl}^- \text{ (solution)}$$

in which Cl (crystal) and Br (crystal) denote the chloride and bromide in the mixed crystals. At equilibrium it is found that

$$K' = \left(\frac{a\ \mathrm{Br}^-}{a\ \mathrm{Cl}^-}\right)_{\text{crystal}} \left(\frac{a\ \mathrm{Cl}^-}{a\ \mathrm{Br}^-}\right)_{\text{solution}} = \left(\frac{f_{\mathrm{Br}^-}\ N_{\mathrm{Br}^-}}{f_{\mathrm{Cl}^-}\ N_{\mathrm{Cl}^-}}\right)_{\text{crystal}} \left(\frac{f_{\mathrm{Cl}^-}\ N_{\mathrm{Cl}^-}}{f_{\mathrm{Br}^-}\ N_{\mathrm{Br}^-}}\right)_{\text{solution}} \qquad (1)$$

in which a represents the activity of the particular component, f the activity coefficient, N the mole fraction. With the justifiable assumption that $f_{\mathrm{Cl}^-} = f_{\mathrm{Br}^-}$ in the solution (or that their ratio is constant over a wide range of ionic strengths) expression (1) can be written as

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(1) From a thesis submitted to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the degree of doctor of philosophy, 1936.

(2) R. B. Wilsey, *J. Franklin Inst.*, **200**, 739 (1925).

(3) F. W. Küster, *Z. anorg. allgem. Chem.*, **19**, 81 (1899).

(4) A. Thiel, *ibid.*, **24**, 1 (1900).

(5) O. Ruff and E. Ascher, *ibid.*, **185**, 369 (1929).

(6) E. D. Eastman and R. T. Milner, *J. Chem. Phys*, **1**, 444 (1933).

$$\left(\frac{\text{moles Br}^-}{\text{moles Cl}^-}\right)_{\text{crystal}} \left(\frac{\text{moles Cl}^-}{\text{moles Br}^-}\right)_{\text{solution}} = K' \left(\frac{f_{\text{Cl}^-}}{f_{\text{Br}^-}}\right)_{\text{crystal}} = K \quad (2)$$

K being called the distribution coefficient.

The value of K calculated by Küster[3] from his experiments was found to vary continuously with the composition of the precipitate. On the basis of equation (2) this variation is attributed to deviations from the ideal state in the solid as exemplified by a variation of the ratio of $(f_{\text{Cl}^-}/f_{\text{Br}^-})$ solid.

The above expressions and the method of approach which are given in the thesis[1] are almost identical with those described by Flood[7a] and Flood and Bruun.[7b] In addition, the latter authors concluded that K is equal to the ratio of the solubility products and equal to K' at a mole ratio of chloride to bromide in the solid of 1.

Experimental

In previous work, mainly that of Küster, analysis of the system was made by filtering off the mixed crystals, and analyzing them by use of the classical indirect gravimetric method—one admittedly inaccurate when the ratio of chloride to bromide is very large or very small. In our experiments, the residual bromide in the aqueous solution was determined by the method of D'Ans and Höfer,[8] with slight modifications.[9] Since the amounts of the various constituents which had been added were known, this allowed the calculation of the compositions of the two phases. This procedure enabled us to analyze with fair accuracy systems in which the gravimetric method would be extremely inaccurate. The reagents used were all reagent grade, ground and dried. The solutions were made up in distilled water and analyzed; the silver nitrate and chloride solutions gravimetrically, the bromide solutions by the above volumetric method. Application of the latter method to the sodium chloride showed that this salt contained less than 0.003% NaBr.[9]

Quite generally the experiments were performed by adding a measured volume of standard silver nitrate to a mixture of a chloride and bromide solution of known composition. After precipitation the solution was made up with water to a known volume and the suspensions shaken for various periods of time. After a given time the bromide content of the solution was determined in the centrifugate. Changes in the order of addition of the reagents have been made in order to see whether the same equilibrium was found when starting under different conditions.

Since Küster[3] did not make sure that he had reached equilibrium (in some experiments he stirred for only two and one-half hours) his experiment number 11 was repeated, adhering closely to his directions but extending the time of shaking from two and one-half hours to one week and analyzing for bromide by our method. Over this period of time the final bromide concentration remained constant (3.6×10^{-3} M), indicating that in this particular case equilibrium was reached within two and one-half hours of shaking. From the results a value of $K = 488$ (19°) was calculated, whereas Küster reported $K = 469$, a satisfactory agreement.

Küster always used a total volume of 1000 ml., whereas in our later work a volume of 100 or 225 ml. of suspension was used. Therefore it was thought desirable to make a few experiments at 19° using a volume of 100 ml. of suspension. After precipitation the suspension was shaken for three days and an aliquot part of the supernatant liquid analyzed for bromide. As an example of the calculations, the composition of the solutions and the derived values are given in Table I. In these cases 25 ml. of 0.2791 M silver nitrate was added to the chloride–bromide mixture.

TABLE I

EQUILIBRIUM AT 19°. TOTAL VOLUME 100 ML.

2 M NaCl, taken, ml.	0.1 M KBr taken, ml.	Millimoles at equilibrium Cl^- in soln.	 Cl^- in ppt.	 Br^- in soln.	 Br^- in ppt.	Mole fraction AgBr in solid	K
25	35	46.4	3.58	0.103	3.40	0.487	428
10	55	18.4	1.60	.115	5.38	.772	538

The corresponding values of K, interpolated from Küster's data, are 410 and 525, respectively. Apparently, there is no appreciable effect of volume changes upon the value of K. A tenfold change in volume resulted in values agreeing within the experimental error. This agreement justifies our assumptions that the variation of K is not to be attributed to a change of the ratio of the activity coefficients of chloride and bromide in solutions but to a change of the ratio in the solid, when the composition of the latter is altered.

Equilibrium at 27 ± 1°

In the first set of experiments a measured volume of 0.2791 M sodium chloride was introduced into a 250-ml. brown glass bottle, then equal volumes of water and of 0.2791 M silver nitrate were added, the latter as the solution was stirred vigorously. After stirring for two minutes, measured volumes of more concentrated sodium chloride and of potassium bromide were added and, if necessary, water to make the volume up to 225 ml. The glass stopper was put in place, sealed in with paraffin and the bottle shaken violently for a given period of time at 27 ± 1°. The bromide concentration in the centrifugate was determined by the volumetric method. For the sake of brevity, only the mole percentages of bromide in the solid, the final bromide concentration in the solution and the values of K after various periods of shaking are reported in Table II. For details about the composition of the original suspension and the analyses the reader is referred to the thesis of the junior author.[1] In all cases equilibrium was established within twenty-four hours of shaking. It should be noted that a small error in the determination of the final bromide concentration has a relatively large effect upon the value of K. This is especially true when the final bromide concentration is extremely small as in series IV where it was of the order of 3×10^{-6} M. At this small concentration the analytical determination is accurate

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(7) (a) H. Flood, *Z. anorg. allgem. Chem.*, **229**, 76 (1936); (b) Flood and B. Bruun, *ibid.*, **229**, 85 (1936).

(8) J. D'Ans and P. Höfer, *Z. angew. Chem.*, **47**, 73 (1934).

(9) I. M. Kolthoff and H. C. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, **9**, 75 (1937).

TABLE II

VALUES OF K AT 27° AFTER VARIOUS PERIODS OF SHAKING

The following figures correspond to the amounts of silver chloride taken and the original chloride concentrations in the various suspensions, the latter having a volume of 225 ml.: I, 1 g., 0.888 *M;* II, 1 g., 0.444 *M;* III, 0.08 g., 0.884 *M;* IV, 1 g., 0.0888 *M;* V, 0.08 g., 0.0884 *M;* VI, 0.08 g., 0.884 *M*.

		I			II			III	
Time of shaking	Bromide concn. in solution, $M \times 10^4$	Mole fraction of AgBr in solid	K	Bromide concn. in solution, $M \times 10^4$	Mole fraction of AgBr in solid	K	Bromide concn. in solution, $M \times 10^4$	Mole fraction of AgBr in solid	K^a
0	22.2	0	...	22.4	0	...	22.1	0	...
1 hour	2.83	0.0622	201	1.98	0.0652	156	15.1	0.286	234
3 hrs.	2.41	.0638	252	1.48	.0667	215			
6 hrs.	2.33	.0642	261						
12 hrs.	2.53	.0635	238						
21 hrs.	2.46	.0636	246	1.24	.0675	260	14.2	.322	296
63 hrs.	2.49	.0635	243	1.30	.0673	247	14.1	.326	308
1 week	2.46	.0638	246	1.28	.0674	252	13.8	.338	327
1 month	2.56	.0634	235				13.8	.338	327
Equilibrium value		.0635	235	1.28	.0674	252		.338	327
		IV			V			VI	
0	2.22	0	...	2.21	0		2.35	0	
1 hour	0.0253	0.00709	250						
3 hrs.	.0228	.00709	287	0.413	0.0725	168	1.66	0.0288	158
6 hrs.									
12 hrs.									
21 hrs.	.0211	.00709	300	.319	.0765	230	1.46	.0371	234
63 hrs.							1.46	.0371	234
1 week	.0257	.00709	246	.301	.0777	245	1.48	.0362	224
1 month	.0311	.00707	204	.308	.0768	239			
Equilibrium value		.00707	204		.0768	239		.0362	224

[a] In Series III and VI the solubility of the small amount of precipitate in the strong sodium chloride solution has been considered. Estimated from the data of Forbes and Cole[10] the solubility of silver chloride in 0.88 *M* sodium chloride is about 7×10^{-5} *M*. Application of a corresponding correction resulted in a change in K of only 3 to 4%. The solubility of the mixed crystals is smaller than that of silver chloride; since the above calculation yielded only a small correction for K it was not necessary to consider the solubility of the mixed crystals instead of that of silver chloride.

to only 10%. With a final bromide concentration of 2×10^{-5} *M* the method is accurate to 1%. Series I was repeated in the presence of nitric acid, the concentration of the acid in the suspension being 0.04 *M*, the same as used by Küster. The time–distribution curve of the bromide was practically identical with that in series IV, the final mole fraction of silver bromide in the solid being 0.00707 and K equal to 227.

Series I was repeated but instead of starting with a fresh precipitate of pure silver chloride the silver nitrate was added to a mixture of 25 ml. 0.2791 *M* sodium chloride, 50 ml. of 0.01 *M* potassium bromide and 25 ml. of water. After precipitation the conditions were made identical with those of series I. The time–distribution curve became practically identical with that of Series I after twenty-four hours; the final mole fraction of silver bromide in the solid being 0.0635 and K equal to 240. Series IV was also repeated in this way—precipitating together the mixture of chloride and bromide. Again, the time–distribution curve was practically identical with that of Series IV, the final mole fraction of silver bromide in the solid being 0.00707 and the final bromide concentration in the solution 2.8×10^{-6} *M* and K equal to 227. From these experiments it is evident that in all cases a true state of equilibrium was reached as the same final values were found, whether the original solid phase was pure silver chloride or a mixed crystal containing virtually all the bromide in the system.

The results of the determination of K at higher mole fractions of silver bromide are reported in Table III. In all cases 25 ml. of 0.2791 *M* silver nitrate corresponding to 1 g. of silver chloride was used as precipitating agent. After mixing of the reagents and making up to the indicated volume with water, the suspensions were shaken for one week at 27 ± 1°, centrifuged and the supernatant solutions analyzed for bromide. Equilibrium was approached from two sides, starting either with fresh silver bromide (a) or silver chloride (b). In all cases, except in the last sets in which the final mole fraction of bromide was very large (0.925), the true state of equilibrium was practically reached after a week of shaking.

With the high mole fraction of bromide in the precipitate true equilibrium was not reached after a month of shaking, although it seems to have been approached closely after one week when starting with silver bromide. In the latter case inhomogeneous mixed crystals too rich in chloride are formed during the early stages of aging as a result of recrystallization. Upon further aging these inhomogeneous crystals recrystallize faster than those formed in the reverse precipitation which soon become too rich in bromide and have a smaller solubility than the mixed crys-

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[10] G. S. Forbes and H. I. Cole, THIS JOURNAL, 43, 2492 (1921).

TABLE III

VALUES OF K AT HIGHER MOLE FRACTIONS OF AgBr (27 ± 1°)

Order of pptn.	Total halide in system Cl⁻, mm.	Total halide in system Br⁻, mm.	Total volume, ml.	Final amt. of bromide in solution, mm.	Mole fraction of AgBr in solid	K	Average of K
a	50	3.5	230	0.1265	0.483	343	343
b	50	3.5	230	.1265	.483	343	
a	50	3.5	100	.121	.484	359	364
b	50	3.5	100	.118	.484	369	
a	20	5.5	230	.1373	.768	443	426
b	20	5.5	230	.1475	.767	410	
a	20	5.5	100	.135	.771	456	441
b	20	5.5	100	.143	.770	426	
a	6.5	6.5	230	.1293	.913	476	476
b	6.5	6.5	230	(.1197)	(.914)	(524)[d]	
a[c]	2.0	6.5	100	.0402	.925	457	457
a[c]	2.0	6.5	100	.0389	.923	473	473
b	2.0	6.5	100	(.0208)	(.925)	(675)[d]	
b[c]	2.0	6.5	100	(.0292)	(.925)	(647)[d]	

[a] Silver nitrate added to the bromide, then chloride added. [b] Silver nitrate added to the chloride, then bromide added. [c] Shaken for one month instead of one week. [d] Not at equilibrium.

tals containing more chloride. Moreover, freshly precipitated silver bromide has a larger surface than a similar precipitate of silver chloride, the larger surface of the former favoring more rapid recrystallization. It may be noticed that in the last four cases reported in Table III the mole fractions of silver bromide in the solid are practically the same. Thus the same value of K would have been found in these four cases, if the analyses had been made according to the indirect method of Küster;[3] evidently the amount of bromide left in the solution is a much more sensitive indicator of the state of equilibrium. In order to ascertain that equilibrium had been reached in most of the experiments previously reported, a series of experiments was run by precipitating the bromide first and performing the shaking for one week in a medium 1 M in ammonia. The latter is a fair solvent for silver halides and hence should promote recrystallization. In the final analyses the amount of dissolved silver was determined by precipitation and weighing as silver iodide and was taken into account in the calculation of the composition of the solid. For the sake of brevity the details[1] are not reported separately, but the results are included in Table IV, the latter giving a summary of all the data found. From the good agreement it may be concluded that the figures reported in Table III and obtained by the method of precipitation "a" (Tables II, III and IV) correspond to the state of true equilibrium and that ammonium does not affect the value of K.

TABLE IV

EQUILIBRIUM VALUES OF K AT 27 ± 1°

Mole fr. of AgBr	0.00707	0.0362	0.0635	0.0674	0.0768
K	204	224	235	252	239
Mole fr. of AgBr	0.102	0.338	0.483	0.697	0.768
K	257[x]	327	354	395[x]	426
Mole fr. of AgBr	0.770	0.913	0.917	0.925	0.923
K	441	476[y]	466[z]	457[y]	473[y,z]

[x] In 1 M ammonia. [y] Silver bromide precipitated first, one week of shaking. [z] One month of shaking.

In Fig. 1 the values of K are plotted against the mole fraction of silver bromide in the solid. Within the experimental error K is found to increase linearly with the mole fraction N_{AgBr} of silver bromide in the solid. The values of K calculated from Küster's data at 19° have also been plotted in a similar way.

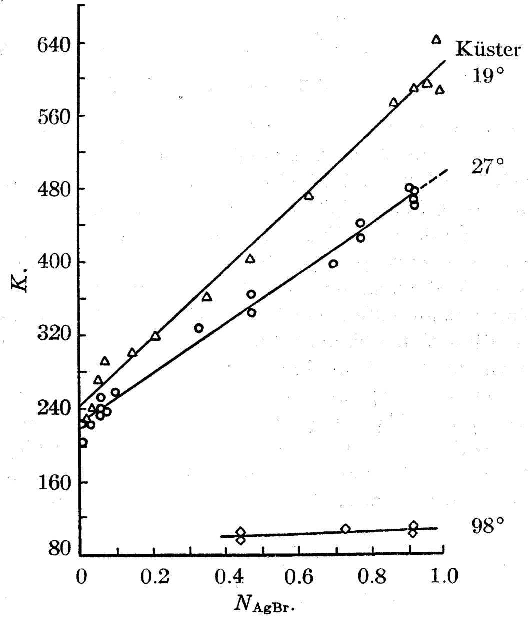

Fig. 1.—Value of K as function of N_{AgBr} at 19 (Küster), 27 and 98°.

The Value of K at 98°.—The experiments were carried out in a similar way to that reported in Table III. Immediately after precipitation and making up to volume, the bottles were heated in a water-bath to 100° (five to ten minutes), stoppered with collodion coated corks and placed in a rotator in an oven held at 98 ± 2° for a week. Then the bottles were cooled, centrifuged and samples taken for analysis for bromide. The results are given in Table V and also plotted in Fig. 1.

TABLE V

EQUILIBRIUM VALUES OF K AT 98 ± 2°. TOTAL VOLUME, 100 ML.

Order of pptn.	Total halide in system Cl⁻, mm.	Total halide in system Br⁻, mm.	Final amt. of bromide in soln. in millimoles	Mole fraction of AgBr in solid	K	$K_{\text{av.}}$
a	50	3.5	0.382	0.447	98	100
b	50	3.5	.367	.448	103	
a	20	5.5	.447	.724	106	106
b	20	5.5	(.397)	(.730)	(124)	
a	2.0	6.5	.139	.913	102	106
b	2.0	6.5	.132	.914	110	

[a] Silver nitrate added to bromide, then chloride added.
[b] Silver nitrate added to chloride, then bromide added.

Evidently, practically the same values were obtained independent of the manner of precipitation, indicating that distribution equilibrium had been obtained in all cases. At mole fractions of silver bromide between 0.45 and 0.91 a constant value of K of 104 ± 4 was found within the experimental error.

TABLE VI

COMPARISON OF K WITH RATIO OF SOLUBILITY PRODUCTS AND SOLUBILITIES OF SILVER CHLORIDE AND BROMIDE

Medium	t, °C.	S. P. AgCl	S. P. AgBr	sol. $\frac{\text{AgCl}}{\text{AgBr}}$	$\frac{\text{S. P. AgCl}}{\text{S. P. AgBr}}$	K	N_{AgBr}
Water	25	1.70×10^{-10}(12,13)	6.4×10^{-13}(12)	16.3	265	374[a]	0.5
						265[a]	.15
Water	100	2.10×10^{-8}(14)	3.25×10^{-10}	8	65	104	.45–0.9
Ethanol	25	1.16×10^{-14}(15)	1.06×10^{-16}				
		0.92×10^{-14}(16)	0.76×10^{-16}	10.8	116	110	.069

[a] Estimated from our data at 27°.

Experiments in Ethanol at 27 ± 2°.—A few experiments were made in absolute ethanol instead of in water as a liquid medium. Silver chloride was precipitated from aqueous medium at 27°, washed with water and then with absolute ethanol. After air had been drawn through to remove most of the adhering liquor the precipitate was divided among several bottles containing 210 ml. of a solution in absolute ethanol, 0.00237 M in sodium bromide and 0.466 M in lithium chloride. The bottles were shaken for various periods of time at 27° and centrifuged. The bromide was determined in the solution and silver in the precipitate. The values of K calculated from the results after various periods of shaking were 27.9 after two hours, 64.4 after a day and 109.5 after nine weeks. The mole fraction of silver bromide in the precipitate after nine weeks was 0.069.

Discussion

1. From the results reported in Table II it is seen that upon shaking of freshly precipitated silver chloride with an aqueous solution containing chloride and bromide a maximum is found in the amount of bromide in the precipitate after a certain period. During the early stages of aging, heterogeneous mixed crystals too rich in bromide are formed which eventually become homogeneous after repeated recrystallizations upon subsequent shaking. Qualitatively, the phenomenon is comparable to the heterogeneous distribution of thorium B through lead sulfate during the early stages of aging of the latter,[11] although in the latter case no maximum was found.

2. If silver chloride and bromide would form an ideal system of solid solutions it is easily derived (compare Flood and Bruun[7]) that under equilibrium conditions

$$\left(\frac{a\ \text{Cl}^-}{a\ \text{Br}^-}\right)_{\text{solution}} \left(\frac{N\ \text{Br}^-}{N\ \text{Cl}^-}\right)_{\text{solid}} = \frac{\text{S. P. AgCl}}{\text{S. P. AgBr}} = K'$$

(compare eq. 1 and 2)

In this equation mole fractions have been written instead of activities in the solid state, whereas S. P. denotes the solubility (activity) product. Actually it is seen from Fig. 1 that at 19 and 27° K increases with increasing mole fraction of bromide in the solid, the slope of the line being less at 27° than at 19°. It appears that the system approaches an ideal one with increasing temperature and it seems to behave as such at 98°.

In Table VI are given the ratios of the solubilities and of the solubility products of silver chloride and bromide in water at 25 and 100° and in ethanol at 25°. In water at 100° and in ethanol at 25° ($N_{\text{AgBr}} = 0.069$) the agreement between K and the ratio of the solubility products is within the experimental error. In water at 27° K is a linear function of the mole fraction of silver bromide in the solid, the value of K found being equal to the ratio of the solubility products at $N_{\text{AgBr}} = 0.15$.

3. Although according to Hildebrand's[17] own statement it is doubtful whether the system silver chloride–bromide can be considered as a "regular solution,"[18] this concept was applied by Flood and Bruun[7] to this particular case. On this basis it was inferred by the latter authors that log K should be a linear function of N_{AgBr}. They plotted log K *versus* $(2N_{\text{AgBr}} - 1)$ for Küster's data and actually found the relation $\log K = 0.19\ (2N_{\text{AgBr}} - 1)$ to hold within the experimental error. Our own data at 27° give a slope of 0.17, although our experimental data fit better the simple relation $K = K_0 + aN$, as plotted in Fig. 1.

Using the equations given by Hildebrand[18] (pp. 69, 70) in describing a regular solution, we may calculate the slope, approximately, in the following way. According to Hildebrand

$$RT \ln a_2/N_2 = bN_1^2 = RT \ln \gamma_2 \qquad (3)$$

$$\overline{H}_1 = bN_2^2;\ \overline{H}_2 = bN_1^2 \qquad (4)$$

in which γ is the activity coefficient, $\overline{H}$ partial

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(11) I. M. Kolthoff and Chas. Rosenblum, THIS JOURNAL, **58**, 116 (1936).

(12) A. S. Brown and D. A. McInnes, *ibid.*, **57**, 459 (1935); W. R. Carmody, *ibid.*, **54**, 188 (1932); E. Neumann, *ibid.*, **54**, 2195 (1932); S. Popoff and E. Neumann, *J. Phys. Chem.*, **34**, 1853 (1930).

(13) A. Thiel, *Z. anorg. allgem. Chem.*, **24**, 57 (1900); K. Hess and K. Jellinek, *Z. physik. Chem.*, **A162**, 153 (1932).

(14) W. Böttger, *ibid.*, **56**, 83 (1906).

(15) A. McFarlane and H. Hartley, *Phil. Mag.*, **13**, 425 (1932).

(16) F. K. V. Koch, *J. Chem. Soc.*, 1551 (1930).

(17) J. H. Hildebrand, "Solubility of Non-electrolytes," A. C. S. Monograph, Second Edition, Reinhold Publishing Corporation, 1936, p. 66.

(18) J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

molal heat of mixing, b a constant, N the mole fraction in the mixed crystal.

From the above relations and the conventional between partial molal quantities it is found that

$$b = H/N_1N_2 \qquad (5)$$

in which H is the heat of mixing per mole.

From equation (2) in the present paper it is found that

$$\log K = \log K' + \log (f_{\text{Cl}}/f_{\text{Br}})_{\text{crystal}} \qquad (6)$$

From Hildebrand's expressions it follows that

$$RT \ln f_{\text{Cl}} = bN^2_{\text{Br}}$$
$$RT \ln f_{\text{Br}} = bN^2_{\text{Cl}}$$

and

$$\log_{10}\left(\frac{f_{\text{Cl}}}{f_{\text{Br}}}\right) = \frac{0.4343b}{RT}(2N_{\text{Br}} - 1) \qquad (7)$$

Combination of equations (6) and (7) leads to

$$\log K = \log K' + \frac{0.434b}{RT}(2N_{\text{Br}} - 1) \qquad (8)$$

Hence, if log K is plotted as a function of $(2N_{\text{AgBr}} - 1)$, the slope of the line should be

$$\frac{0.4343b}{RT} = \frac{0.4343}{RT}\,\frac{H}{N_1N_2}$$

Eastman and Milner[6] give the change in heat content in the formation of one mole of a mixed crystal, in which $N_{\text{AgBr}} = 0.728$ and $N_{\text{AgCl}} = 0.272$ as 81 ± 10 calories.

Taking this as the heat of mixing the calculated slope is

$$\frac{0.4343}{1.99 \times 298} \times \frac{81}{0.728 \times .272} = 0.30 \pm 0.04$$

The calculated value deviates from the experimentally found slope (0.19 Küster, 18°; 0.17 Yutzy and Kolthoff, 27°) by more than the estimated error. Thus the consideration of the solid phase as a "regular solution" seems questionable.

Summary

1. The distribution coefficient K of bromide between solution and mixed crystals of silver chloride and bromide has been determined at 27 and 98° in aqueous medium and at one mole fraction of silver bromide in ethanol at 27°.

2. At 27° K changes as a linear function of the mole fraction of silver bromide in the solid. Evidence has been given that the mixed crystals cannot be considered as "regular solutions." At 98° the value of K becomes practically independent of N_{AgBr}, and the solid approaches the behavior of an ideal solution.

3. The value of K is approximately equal to the ratio of the solubility products as pointed out by Flood and Bruun[7] and not to the ratio of the solubilities of the components.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 1, 1937

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

The Heat Capacity of Silver Nitrite from 15 to 300°K. The Heat of Solution at 298°K. of Silver Nitrite, Barium Nitrate and Thallous Nitrate. The Entropy of Silver Nitrite, Thallous Ion, Nitrate Ion and Nitrite Ion

BY OLIVER L. I. BROWN, WENDELL V. SMITH AND WENDELL M. LATIMER

The determination of the entropy of silver nitrite enables a calculation to be made of the entropies of both nitrate and nitrite ions. The entropy of nitrate ion can also be obtained by three other independent methods, making use of existing data on sodium nitrate, potassium nitrate and barium nitrate, combined with a value of the heat of solution obtained in this investigation. In the present paper we shall also present two methods of calculating the entropy of thallous ion.

Material.—The silver nitrite was a C. P. sample prepared in this Laboratory. It was recrystallized from distilled water and the product dried in a vacuum desiccator for several days. The final product was analyzed for nitrite by titration with permanganate solution, and for silver by thermal decomposition. Calcd. Ag, 70.10; nitrite, 29.90. Found: Ag, 69.89, 69.95, 69.90, 69.96; nitrite, 29.79, 29.74. The barium nitrate was a Mallinckrodt reagent grade sample, which was dried and used without further purification. The thallous nitrate was the same as that used by Latimer and Ahlberg.[1]

Heat Capacity Measurements.—The experimental method followed the general procedure described by Latimer and Greensfelder.[2] Specific

[1] Latimer and Ahlberg, THIS JOURNAL, **54**, 1900 (1932).

[2] Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).

Table I

Molal Heat Capacity of Silver Nitrite

T, °K.	C_p, cal./mole/deg.	T, °K.	C_p, cal./mole/deg.	T, °K.	C_p, cal./mole/deg.
14.36	1.56	72.32	10.58	189.00	16.77
15.77	1.83	77.10	11.04	195.94	17.04
17.09	2.07	82.86	11.59	202.25	17.29
19.21	2.46	89.26	12.10	215.27	17.53
21.65	2.85	94.07	12.56	223.49	17.67
23.84	3.22	107.35	13.40	232.36	17.91
26.32	3.72	113.53	13.72	240.05	18.15
28.82	4.17	124.51	14.22	248.24	18.34
31.24	4.60	129.71	14.54	255.45	18.54
37.72	5.83	135.02	14.84	260.44	18.57
41.04	6.40	140.48	15.13	265.92	18.87
44.15	6.88	145.93	15.31	273.93	18.83
47.40	7.35	151.31	15.51	274.16	18.86
51.67	8.02	156.59	15.68	284.13	18.96
56.73	8.76	156.60	15.68	284.30	18.84
62.21	9.41	163.45	15.92	294.94	18.67
67.37	10.00	174.86	16.24		

heat measurements were made on a sample weighing 103.893 g. *in vacuo* (0.67511 mole). One calorie was taken equal to 4.1833 int. joules. The heat capacities near the melting point of water showed the presence of 0.12% of water in the sample, in spite of the precautions taken to exclude it. The final heat capacities were corrected for this amount of water, even though the correction was small.[3] The results are summarized in Table I, and shown graphically in Fig. 1.

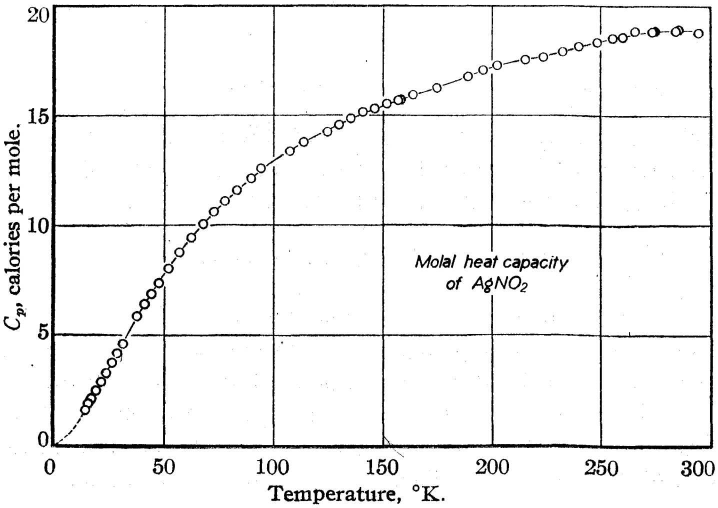

Fig. 1.—Molal heat capacity of silver nitrite.

Entropy of Silver Nitrite.—The entropy of silver nitrite at 298.1°K. was evaluated by graphical integration of the heat capacity data, combined with an analytical integration between 0° and 14.36° using the Debye specific heat equation. The result is summarized in Table II.

Table II

Molal Entropy of Silver Nitrite

0–14.36°K.	Debye extrapolation	0.55
14.36–298.1°K.	Graphical from data	30.07 ± 0.1
	Entropy at 298.1°K.	30.62 e. u.

Heat of Solution of Silver Nitrite.—We wish to acknowledge our indebtedness to Mr. Kenneth S. Pitzer whose work has enabled us to obtain an accurate value for this heat of solution. The work of Abegg and Pick[4] indicates that silver nitrite is not completely dissociated even in dilute solution so that a direct determination of the heat of solution does not give the quantity desired because of the very large uncertainty in the heat of dissociation and dilution. However, the heat of solution at infinite dilution can be obtained from the following three heats: (1) the heat of solution of silver nitrite in a dilute ammonia solution, (2) the heat of solution of silver nitrate in the dilute ammonia solution, and (3) the heat of solution of silver nitrate in an infinite amount of water. Adding (1) and (3) and subtracting (2) gives the heat of solution of silver nitrite in an infinite amount of water if one assumes that the heat effect going from nitrite ion in dilute ammonia solution to nitrite ion in an infinite amount of water is the same as that for nitrate ion. The heat of solution of silver nitrite in 0.14 *M* ammonia to form a 0.01 *M* solution was found to be −8020 ± 60 cal. Combining this with the heats for the other reactions[5] the heat of solution of silver nitrite at infinite dilution is found to be 10,070 ± 100 cal.

Entropy of Nitrite Ion.—Abegg and Pick[4] determined the solubility of silver nitrite at 298.1°K. and found a value of 2.0×10^{-4} for the equilibrium constant, from which $\Delta F^\circ_{298.1}$ of solution is 5050 cal. The entropy of solution is, therefore, $\Delta S^\circ = (10{,}070 - 5050)/298.1 = 16.8$ e. u. The entropy of silver ion[6] is 18.4, so that the entropy of nitrite ion is $S^\circ = 30.6 + 16.8 - 18.4 = 29.0$ e. u.

Heat of Solution of Barium Nitrate and Thallous Nitrate.—The integral heat of solution of

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(3) A discussion of this correction is given by Brown, Smith and Latimer, *ibid.*, **58**, 2144 (1936).

(4) Abegg and Pick, *Z. anorg. Chem.*, **51**, 1 (1906).

(5) Smith, Brown and Pitzer, to be published.

(6) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 89 (1934).

barium nitrate in 614 moles of water at 298.1°K. was determined using the calorimeter previously described.[7] Two determinations gave 9256 and 9236 cal. per mole. Combining the average value with the known heat of dilution,[8] the heat of solution at infinite dilution was found to be 9496 cal. per mole. We are greatly indebted to Mr. Kenneth S. Pitzer who has measured the heat of solution of thallous nitrate in 5000 moles of water at 298.1°K. and found a value of 10,050 ± 50 cal. per mole. Combining this value with an estimated heat of dilution we find the heat of solution at infinite dilution to be 10,020 cal. per mole.

Entropy of Nitrate Ion.—The reaction

$$2AgNO_2(s) = Ag^+ + NO_3^- + Ag(s) + NO(g) \quad (1)$$

has been studied by Abegg and Pick[4] and by Lewis and Adams.[9] The free energy change in this reaction at 298.1°K. has been fairly well established by these workers, but the $\Delta H°$ of the reaction which is necessary in computing the entropy change was not known with sufficient accuracy. Consequently, Randall, Manov and Brown[10] have studied the equilibrium reaction (2) and from the

$$2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g) \quad (2)$$

change of equilibrium pressure with temperature have determined the $\Delta H^\circ_{298.1}$ of reaction (2) to be 14,040 cal. Combining this with the heat of solution of silver nitrate in an infinite amount of water[5] 5360 ± 50 cal./mole we find $\Delta H^\circ_{298.1}$ for reaction (1) to be 19,400 cal./mole. An extrapolation of the equilibrium measurements of Lewis and Adams and Abegg and Pick yields an average $\Delta F^\circ_{298.1} = 3600$. The entropies of nitric oxide,[11] silver,[12] and silver ion[6] are 50.4, 10.2 and 18.4 e. u., respectively, so that the entropy change of the reaction, and the entropy of nitrate ion are given by the expressions

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = (19{,}400 - 3600)/298.1 = 53.0 \text{ e. u.}$$

$$S^\circ_{NO_3^-} = \Delta S^\circ + 2S^\circ_{AgNO_2} - S^\circ_{Ag} - S^\circ_{Ag^+} - S^\circ_{NO(g)} = 35.2$$

Latimer and Ahlberg[13] determined the entropy of barium nitrate and calculated the entropy of nitrate ion. The principal uncertainties in their calculation were the entropy of barium ion, and the heat of solution of barium nitrate. The entropy of barium ion has recently been more accurately evaluated,[7] and with the heat of solution determined as described above, permits an accurate calculation of the entropy of nitrate ion. The entropy of solution and the entropy of nitrate ion are given by the expressions

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = (9496 - 3200)/298.1 = 21.1 \text{ e. u.}$$

$$S^\circ_{NO_3^-} = {}^1/_2(\Delta S^\circ + S^\circ_{Ba(NO_3)_2} - S^\circ_{Ba^{++}}) = {}^1/_2(21.1 + 51.1 - 2.2) = 35.0 \text{ e. u.}$$

The entropy of nitrate ion can be determined by a third independent method. The entropy of sodium nitrate[14] is 27.87 ± 0.08 e. u. The activity coefficient of sodium nitrate[15] at saturation (10.83 *M*) and a temperature of 298.1°K. is 0.355. The free energy of solution is then $\Delta F^\circ_{298.1} = -1363.8 \log (10.83 \times 0.355)^2 = -1596$ cal./mole. The heat of solution of sodium nitrate in an infinite amount of water at 291.1°K. is given by Bichowsky and Rossini[16] as 5051 cal./mole. Correcting this value to 298.1, using Rossini's[17] value for the partial molal heat capacity of sodium nitrate, we obtain $\Delta H^\circ_{298.1} = 4810$ cal./mole. The entropy of sodium ion[6] is 14.7 e. u., so that the entropy of solution and the entropy of nitrate ion are given by the expressions

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = (4870 + 1596)/298.1 = 21.5$$

$$S^\circ_{NO_3} = \Delta S^\circ + S^\circ_{NaNO_3} - S^\circ_{Na^+} = 21.7 + 27.9 - 14.7 = 34.7 \text{ e. u.}$$

The entropy of nitrate ion can be determined by still another method, which is independent of the three already described. The entropy of potassium nitrate[14] is 31.77 ± 0.10 e. u. The solubility in water[18] at 298.1°K. is 3.74 *M*, while the activity coefficient[19] at saturation is 0.233. The free energy of solution is then $\Delta F^\circ_{298.1} = 163$ cal./mole. The heat of solution in an infinite amount of water[16] at 291.1°K. is 8633 cal./mole. Correcting this value to 298.1°K., using Rossini's[17] value for the partial molal heat capacity of potassium nitrate, we obtain $\Delta H^\circ_{298.1} = 8341$ cal./mole. The entropy of potassium ion[3] is 24.2 e. u., so that the entropy of solution and the entropy of nitrate ion are given by the expressions

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = (8341 - 163)/298.1 = 27.4$$

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[7] Brown, Smith and Latimer, THIS JOURNAL, **58**, 1758 (1936).

[8] Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

[9] Lewis and Adams, THIS JOURNAL, **37**, 2308 (1915).

[10] Randall, Manov and Brown, unpublished data.

[11] Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).

[12] Kelley, Bull. 350, Bur. of Mines, 1932.

[13] Latimer and Ahlberg, *Z. physik. Chem.*, Abt. A, **148** (6), 464 (1930).

[14] Southard and Nelson, THIS JOURNAL, **55**, 4865 (1933).

[15] William H. Hopson, Ph.D. Dissertation, State University of Iowa, 1935. Vapor pressures of aqueous solutions of sodium nitrate at 25°.

[16] Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Co., New York, 1936, p. 142.

[17] Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

[18] "International Critical Tables," McGraw-Hill Book Co., Inc New York, 1923.

[19] Robinson, THIS JOURNAL, **57**, 1165 (1935).

$$S_{NO_3^-} = \Delta S^\circ + S^\circ_{KNO_3} - S^\circ_{K^+} = 27.4 + 31.8 - 24.2 = 35.0 \text{ e. u.}$$

The average value of $S^\circ_{NO_3^-}$ is then 35.0 ± 0.1 e. u.

The Entropy of Thallium Ion.—Latimer and Ahlberg[20] determined the entropy of thallous nitrate and calculated a value for nitrate ion. Since the entropy of nitrate ion is now known with greater exactness than the entropy of thallous ion, and particularly since any large uncertainty in the heat of solution of thallous nitrate has been removed by the measurements of Mr. K. S. Pitzer referred to above, we believe it preferable to calculate a value for the entropy of thallous ion. The entropy of solution of thallous nitrate and the entropy of thallous ion are given by the expressions

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = (10{,}020 - 1790)/298.1 = 27.6 \text{ e. u.}$$

$$S^\circ_{Tl^+} = \Delta S^\circ + S^\circ_{TlNO_3} - S^\circ_{NO_3^-} = 27.6 + 38.1 - 35.0 = 30.7$$

Another value for the entropy of thallous ion can be calculated from the electromotive force measurements of Cowperthwaite, La Mer and Barksdale.[21] These authors find for the reaction

$$\text{Tl(s)} + \text{AgCl(s)} = \text{Ag(s)} + \text{Tl}^+ + \text{Cl}^-,\ \Delta F^\circ_{298.1} = -12{,}877 \text{ cal.},\ \Delta H^\circ_{298.1} = -8307 \text{ cal.}$$

The entropies of Tl(s),[12] AgCl(s),[12] Ag(s),[12] and Cl$^-$[6] are, respectively, 15.5 ± 0.1, 23.0 ± 0.1, 10.2 ± 0.1 and 13.5 ± 0.1 e. u. The entropy change of the reaction and the entropy of thallous ion are given by the expressions

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = (-8307 + 12{,}877)/298.1 = 15.3$$

$$S^\circ_{Tl^+} = \Delta S^\circ + S^\circ_{Tl(s)} + S^\circ_{AgCl(s)} - S^\circ_{Ag(s)} - S^\circ_{Cl^-} = 15.3 + 15.5 + 23.0 - 10.2 - 13.5 = 30.1 \text{ e. u.}$$

The values previously calculated for thallous ion[6] have involved considerably greater uncertainties in the entropy and heat of reaction data than the two values calculated here. We therefore recommend the average value $S^\circ_{Tl^+} = 30.4$ e. u.

The Free Energy of Nitrate Ion.—Since the heat of formation of nitrate ion has been determined with considerable accuracy,[22] it can be combined with the entropy of formation to obtain a reliable value for the free energy of formation. Becker and Roth obtain −49,020 ± 80 cal. for the heat of formation from the elements at 293°K. of one mole of nitric acid in 1079 moles of water. Correcting this to infinite dilution and 25° gives $\Delta H^\circ_{298.1} = -49{,}290$ cal. for the heat of formation of nitrate ion. The entropy of formation of nitric acid at 25° is

$$\Delta S^\circ = S_{H^+} + S_{NO_3^-} - \frac{1}{2} S_{N_2} - \frac{3}{2} S_{O_2} - \frac{1}{2} S_{H_2} =$$

$$0 + 35.0 - \frac{1}{2}\,45.79^{23} - \frac{3}{2}\,49.03^{24} - \frac{1}{2}\,31.23^{25} = -77.1$$

Thus, the free energy of formation of nitrate ion from its elements is $\Delta F^\circ_{298.1} = -26{,}310 \pm 90$ cal. The value given by Lewis and Randall[26] is −26,500 cal., which agrees with our value within the limits of accuracy of their calculation.

Summary

The heat capacity of silver nitrite has been determined from 15 to 300°K. The entropy of silver nitrite has been calculated at 298.1°K. The entropy of nitrite ion has been determined as 29.0 e. u. The entropy of nitrate ion has been calculated by four independent methods and the values 35.2, 35.0, 34.7 and 35.0 e. u. obtained. The entropy of thallous ion has been calculated by two independent methods and the values 30.7 and 30.1 e. u. obtained. The heats of solution of silver nitrite, barium nitrate and thallous nitrate at 298.1°K. have been determined. The free energy of formation of nitrate ion at 298.1°K. has been calculated to be −26,310 cal.

Berkeley, Calif. Received March 1, 1937

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[20] Latimer and Ahlberg, This Journal, **54**, 1903 (1932).

[21] Cowperthwaite, La Mer and Barksdale, *ibid.*, **56**, 544 (1934).

[22] Becker and Roth, *Z. Elektrochem.*, **40**, 836 (1934).

[23] Giauque and Clayton, This Journal, **55**, 4875 (1933).

[24] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

[25] Giauque, *ibid.*, **52**, 4816 (1930).

[26] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Diarsyls. IX. Tetra-(3-amino-4-hydroxyphenyl)-diarsyl

BY F. F. BLICKE, J. F. ONETO[1] AND G. L. WEBSTER[2]

The preparation and properties of tetra-(3-amino-4-hydroxyphenyl)-diarsyl $[(H_2N)(HO)C_6H_3]_2As—As[C_6H_3(OH)(NH_2)]_2$ are of special interest because of the structural analogy of this compound with salvarsan $(H_2N)(HO)C_6H_3As{=}AsC_6H_3(OH)(NH_2)$. Fargher[3] isolated and analyzed the diarsyl dihydrochloride and this substance is mentioned also by Christiansen.[4] This paper deals with a study of the diarsyl base, the preparation of the corresponding arsinic acid and several related acids.

Tetra-(3-amino-4-hydroxyphenyl)-diarsyl is insoluble in many of the common organic solvents but is soluble in alkali and acids. In the solid state the diarsyl is quite stable toward oxygen but an alkaline solution of the compound absorbs the gas quite rapidly.

Through the courtesy of Parke, Davis and Company the compounds mentioned below were tested for general toxicity by intravenous injection in white rats and for trypanocidal action against the common *T. equiperdum.*

3,3′-Diamino-4,4′-dihydroxydiphenylarsinic acid (I) failed to kill rats in doses as large as 1500 mg. per kilo body weight, hence it is a relatively non-toxic substance. The corresponding oxide, tetra-(3-amino-4-hydroxyphenyl)-arsyl oxide (II), is much more toxic. Neither compound seemed to be of any value as a trypanocide.

As far as tetra-(3-amino-4-hydroxyphenyl) diarsyl tetrahydrochloride (III), methyl-3-amino-4-hydroxyphenylarsinic acid,[5] methyl-3-amino-4-hydroxyphenylchloroarsine hydrochloride[6] and dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl dihydrochloride[7] are concerned only the first mentioned compound exhibited any appreciable activity as a curative agent against *T. equiperdum* in white rats.

The well-known therapeutic agents 3-acetylamino-4-hydroxyphenylarsonic acid (stovarsol), 3-amino-4-hydroxyphenylarsine oxide hydrochloride (mapharsen) and 3,3′-diamino-4,4′-dihydroxyarsenobenzene (salvarsan) are the *mono* aryl analogs of compounds I, II and III, respectively. In view of the data obtained it seems that no improvement is made, as far as trypanocidal action is concerned, by the attachment of a second aminohydroxyphenyl nucleus to the arsenic atom.

No thorough pharmacological study of any of the compounds was made nor were they tested against spirochetes since the preliminary investigation indicated that they would be of little practical value.

Experimental Part

4,4′-Dihydroxydiphenylarsinic Acid.—This acid, which melted at 246–247° with effervescence,[8] dissolved in hot acetic acid, is decomposed by bromine with the formation of tribromophenol; suspended in acetic acid the arsinic acid is converted quantitatively into arsenic triiodide upon the addition of hydriodic acid.

Anal. Calcd. for $C_{12}H_{11}O_4As$: As, 25.48. Found: As, 25.34.

Di-(3-nitro-4-hydroxyphenyl)-chloro- and -bromoarsine.—Two grams of 3,3′-dinitro-4,4′-dihydroxydiphenyl arsinic acid, prepared by nitration[9] of 4,4′-dihydroxydiphenylarsinic acid, was dissolved in a mixture of 10 cc. of acetic acid, 25 cc. of hydrochloric acid and a drop of hydriodic acid and treated with sulfur dioxide. The gummy precipitate soon solidified; yield 2.1 g. After recrystallization from acetic acid the yellow crystals melted at 142–143°. The product dissolved in dilute sodium hydroxide to yield a red solution.

Anal. Calcd. for $C_{12}H_8O_6N_2AsCl$: As, 19.38; Cl, 9.17. Found: As, 19.46; Cl, 8.67.

The yellow, crystalline bromoarsine, prepared from 1 g. of the arsinic acid, 5 cc. of acetic acid, 11 cc. of hydrobromic acid, a drop of hydriodic acid and sulfur dioxide, melted at 131–132° after recrystallization from acetic acid.

Anal. Calcd. for $C_{12}H_8O_6N_2AsBr$: As, 17.39; Br, 18.55. Found: As, 17.43; Br, 18.65.

3,3′-Diamino-4,4′-dihydroxydiphenylarsinic Acid.—A solution of 200 g. of flake sodium hydroxide in 300 cc. of water was added to 170 g. of ferrous sulfate, dissolved in 500 cc. of water. After the mixture had been shaken thoroughly and cooled, there was added 20 g. of 3,3′-dinitro-4,4′-dihydroxydiphenylarsinic acid, dissolved in

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[1] Parke, Davis and Company Fellow.

[2] University Fellow in the Horace H. Rackham School of Graduate Studies.

[3] Fargher, *J. Chem. Soc.*, **115**, 987 (1919).

[4] Christiansen, THIS JOURNAL, **43**, 374 (1921).

[5] Bertheim, *Ber.*, **48**, 358 (1915); Blicke and Webster, THIS JOURNAL, **59**, 535 (1937).

[6] Blicke and Webster, *ibid.*, **59**, 535 (1937).

[7] Bertheim, *Ber.*, **48**, 358 (1915); Blicke and Webster, THIS JOURNAL, **59**, 539 (1937).

[8] Benda [*Ber.*, **41**, 2371 (1908)], m. p. 239°; Fargher [*J. Chem. Soc.*, **115**, 986 (1919)], m. p. 259°, corr.; Jacobs and Heidelberger [THIS JOURNAL, **41**, 1448 (1919)], m. p. 250–251°. See also Yang and Wang, *J. Chinese Chem. Soc.*, 5, 89 (1937).

[9] Fargher, *J. Chem. Soc.*, **115**, 986 (1919).

100 cc. of water and 9 g. of flake sodium hydroxide. The mixture was shaken again and after one hour was filtered. Hydrochloric acid (about 260 cc.) was added to the filtrate until the latter was slightly acid toward litmus, the precipitated impurities removed by filtration, the light brown filtrate treated with hydrochloric acid, drop by drop, to precipitate the last traces of colored by-products, charcoal added and the mixture filtered again. The filtrate should now be slightly yellow and if the arsinic acid does not begin to precipitate after a short time, a few more drops of acid should be added; yield 9–11 g. of light brown, glistening crystals. When heated the acid darkens about 210° and decomposes at 218°.[10] About 100 cc. of boiling water is required to recrystallize 1 g. of the arsinic acid.

Anal. Calcd. for $C_{12}H_{13}O_4N_2As$: As, 23.12. Found: As, 23.29.

Di-(3-amino-4-hydroxyphenyl)-chlorarsine Dihydrochloride.—A solution prepared from 2.5 g. of 3,3′-diamino-4,4′-dihydroxydiphenylarsinic acid, 6 cc. of water, 20 cc. of hydrochloric acid and a drop of hydriodic acid, was treated with sulfur dioxide. The precipitated chloride dihydrochloride was filtered through a Jena filter, dissolved in the least possible amount of warm water, shaken with charcoal, filtered, the colorless filtrate cooled with ice and the dihydrochloride precipitated by the addition of fuming hydrochloric acid. The pearly flakes weighed 1.9 g.; m. p. 214–215°.[11]

Anal. Calcd. for $C_{12}H_{14}O_2N_2AsCl_3$: As, 18.76; Cl, 26.62. Found: As, 18.65; Cl, 26.61.

Tetra-(3-amino-4-hydroxyphenyl)-arsyl Oxide.—To 5 g. of the above-mentioned dihydrochloride, dissolved in 35 cc. of water, there was added, slowly, 5 g. of sodium hydroxide, dissolved in 15 cc. of water. The clear, alkaline solution was then treated, gradually, with just enough acetic acid (about 3.3 cc.) to precipitate the arsyl oxide. The crystalline oxide is soluble in 0.5 *N* hydrochloric acid, 0.5 *N* sodium hydroxide, alcohol, somewhat soluble in water and insoluble in ether; m. p. 152–155° with decomposition.

Anal. Calcd. for $C_{24}H_{24}O_5N_4As_2$: As, 25.06. Found: As, 24.75.

Tetra-(3-amino-4-hydroxyphenyl)-diarsyl.—Three grams of either 3,3′-diamino-4,4′-dihydroxydiphenylarsinic acid or tetra-(3-amino-4-hydroxyphenyl)-arsyl oxide was dissolved in 30 cc. of 50% hypophosphorous acid, a drop of hydriodic acid added and the solution heated in a modified radical apparatus[12] for one hour at 60°. Upon the addition of 38 cc. of 20% sodium hydroxide solution a copious, crystalline precipitate formed; during the addition of the alkali the mixture should be allowed to become hot, otherwise the precipitate tends to separate in a flocculent state. After the addition of 100 cc. of water the product was filtered and washed three times with 100-cc. portions of water and then several times with acetone; when heated in a sealed tube filled with nitrogen the material turns brown at about 200° and melts suddenly, with decomposition, at 202°. This compound seems to be a tetrahypophosphite of the diarsyl.

Anal. Calcd. for $C_{24}H_{24}O_4N_4As_2 \cdot 4H_3PO_2$: As, 17.71. Found: As, 17.83.

In order to obtain the free diarsyl the salt mentioned above was dissolved in 15 cc. of hot, 20% sodium hydroxide solution; upon the addition of 25% acetic acid until the mixture was acidic toward phenolphthalein the diarsyl precipitated. The liquid was decanted and the diarsyl washed with acetone; yield 1.9 g.; m. p. 193–194° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{24}H_{24}O_4N_4As_2$: As, 25.74. Found: As, 25.51.

The diarsyl is insoluble or only slightly soluble in benzene, ether, acetone, alcohol, chloroform, bromobenzene, acetophenone, ethylene bromide, nitrobenzene, tetralin and acetic acid; it is soluble in pyridine, 50% acetic acid, dilute sodium hydroxide and dilute hydrochloric acid.

The tetrahydrochloride of the diarsyl was prepared in the following manner. The diarsyl obtained from 5.0 g. of 3,3′-diamino-4,4′dihydroxydiphenylarsinic acid was dissolved, while still moist, in a mixture of 3 cc. of concd. hydrochloric acid and 5 cc. of water. After the addition of 100 cc. of alcohol the solvents were removed at 35° under diminished pressure. To the moist, gelatinous salt, dissolved in 17 cc. of absolute alcohol, there was added 40 cc. of ether whereupon the hydrochloride separated in the form of granular crystals. The alcohol and ether were removed under diminished pressure and the residue washed three times with 40 cc. of ether; after the salt had been dried and isolated in a carbon dioxide atmosphere it melted at 170–172°[13] in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{24}H_{28}O_4N_4Cl_4As_2$: As, 20.58. Found: As, 20.13.

Dissolved in 20 cc. of water 0.5884 g. of the diarsyl tetrahydrochloride absorbed little or no oxygen in ten minutes. When sufficient 0.5 *N* sodium hydroxide solution (14 cc.) was added to form the tetra salt of the diarsyl, 10 cc. (N. T. P.) of the gas was absorbed in two minutes and after thirty-five minutes 37 cc. of oxygen had been absorbed.

4,4′-Dimethoxydiphenylarsinic Acid.—To a hot, aqueous suspension of 1 g. of 4,4′-dimethoxydiphenylbromoarsine,[14] stirred vigorously, there was added an aqueous solution of potassium permanganate until the latter was no longer decolorized; any excess of permanganate was reduced with alcohol. The mixture was filtered and the filtrate acidified to congo red; yield 0.7 g. of dimethoxy acid, m. p. 190–191° after recrystallization from acetic acid or water.

Anal. Calcd. for $C_{14}H_{15}O_4As$: As, 23.26. Found: As, 23.28.

In a second procedure the bromoarsine was suspended in hot 10% sodium hydroxide solution and treated with superoxol. After some time the material all dissolved. The arsinic acid precipitated when the solution was acidified.

When 1 g. of the arsinic acid, 4 cc. of acetic acid, 8 cc. of hydrobromic acid (48%) and a drop of hydriodic acid

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[10] Fargher[3] prepared the diamino acid by reduction of the dinitroarsinic acid with sodium hyposulfite but did not report a melting point.

[11] Fargher,[3] who prepared this compound in low yield by another method, reported the melting point to be 215° (corr.).

[12] Blicke and Webster, This Journal, **59**, 538 (1937).

[13] Fargher did not report the melting point of his hydrochloride which he prepared by another method.

[14] Blicke and Smith, *ibid.*, **51**, 1565 (1929).

was treated with sulfur dioxide the bromoarsine formed melted at 63–64°[15] after recrystallization from absolute alcohol. The bromoarsine was converted into tetra-(4-methoxyphenyl)-arsyl oxide when it was warmed for a short time with ammonia water; the oxide melted at 132–134°[16] after recrystallization from petroleum ether (90–100°).

3,3′ - Dinitro - 4,4′ - dimethoxydiphenylarsinic Acid.—Twelve grams of 4,4′-dimethoxydiphenylarsinic acid was nitrated in the same manner as the corresponding dihydroxy acid; yield 12.6 g. of the dinitro acid. The compound was recrystallized from acetic acid; when heated it softened about 220° and melted at 231° with decomposition.

Anal. Calcd. for $C_{14}H_{13}O_6N_2As$: As, 18.18. Found: As, 17.73.

3,3′ - Diamino - 4,4′ - dimethoxydiphenylarsinic Acid.—Ferrous hydroxide was prepared by the addition of 9.5 g. of 70% sodium hydroxide, dissolved in 36 cc. of water, to 23 g. of ferrous sulfate, dissolved in 66 cc. of water; 2 g. of the dinitro acid, dissolved in 20 cc. of water and 1.6 g. of sodium hydroxide, was added. After several hours the mixture was filtered, the filtrate shaken with charcoal, filtered and the filtrate acidified with acetic acid; yield 1.4 g.; the glistening crystals melted at 183–184° with decomposition after recrystallization from water.

Anal. Calcd. for $C_{14}H_{17}O_4N_2As$: As, 21.28. Found: As, 21.27.

Summary

A detailed study has been made of tetra-(3-amino-4-hydroxyphenyl)-diarsyl.

The preparation of 4,4′-dimethoxydiphenylarsinic acid and of 3,3′-diamino-4,4′-dihydroxydiphenylarsinic acid and some of their derivatives has been described.

ANN ARBOR, MICHIGAN RECEIVED MARCH 2, 1937

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[15] Prepared by a different method Blicke and Smith[14] found the melting point to be 60–62°.

[16] Michaelis and Weitz [*Ber.*, **20**, 50 (1887)] obtained the oxide by a different procedure and recorded the melting point as 130°.

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, UNITED STATES DEPARTMENT OF AGRICULTURE]

Quassin. I. The Preparation and Purification of Quassin and Neoquassin, with Information Concerning their Molecular Formulas

BY E. P. CLARK

The bitter and presumably the physiologically active constituent of quassia wood or Surinam wood (*Quassia amara*) is known as quassin. This material was first obtained in crystalline form by Winckler[1] in 1835. Although it has since been investigated by others, little information of value concerning its nature has emerged; in fact, instead of clarifying the problem, these investigations have tended to confuse it.

The principal contributions to the subject have been made by Wiggers,[2] Christensen,[3] Oliveri and Denaro,[4] Oliveri,[5] and Massute.[6] As Christensen and Massute give comprehensive reviews of the subject, the present discussion will present only a résumé of the essential claims concerning the material.

Wiggers, the first to analyze quassin, found it to have 65.8% carbon and 6.94% hydrogen (recalculated on the basis of present atomic weight values). Christensen, who undoubtedly had a pure material, recorded its melting point as 205°, $[\alpha]^{18}\text{D}$ as +37.8° (*C*, 4.22 in chloroform), and its analysis according to the average of three combustions as 66.9% carbon and 7.44% hydrogen. He proposed the molecular formula $C_{31}H_{42}O_9$ for the material, and showed conclusively that it was not a glucoside. Finally, by boiling quassin for twelve hours with 3% sulfuric acid, he obtained a product which melted at 237° and gave upon combustion 66.87% carbon and 6.72% hydrogen.

Oliveri and Denaro had a material that melted at 210–211°, but in view of information which will be presented later they obviously had a mixture of several crystalline substances. They proposed the molecular formula $C_{32}H_{42}O_{10}$ or $C_{16}H_{22}O_5$ for their quassin, and claimed the formation of several anhydrides as the result of the action of dilute sulfuric acid and of acetic anhydride and sodium acetate upon their material. By heating quassin with concentrated hydrochloric acid in a sealed tube, they obtained methyl chloride and a crystalline material to which they assigned the formula $C_{28}H_{38}O_6(COOH)_2$, and which they called quassic acid. On the basis

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(1) F. L. Winckler, *Repert. pharm.*, [2] **4**, 85 (1835); **15**, 74 (1838).

(2) A. Wiggers, *Ann.*, **21**, 40 (1837).

(3) A. Christensen, *Arch. Pharm.*, **220**, 481 (1882).

(4) V. Oliveri and A. Denaro, *Gazz. chim. ital.*, **14**, 1 (1884); **15**, 6 (1885).

(5) V. Oliveri, *ibid.*, **17**, 570 (1887); **18**, 169 (1888).

(6) F. Massute, *Arch. Pharm.*, **228**, 147 (1890).

of these findings and some incomplete work, they stated that quassin had four hydroxyl groups, two carboxymethyl groups and two ketonic groups, and that the molecule had an anthraquinone skeleton.

Massute separated his crude quassin into several fractions having different melting points and assumed them to be homologs differing by various multiples of CH_2, as $C_{32}H_4O_1(CH_2)_3$ and $C_{32}H_4O_1(CH_2)_5$. He made no molecular weight determinations, although methods were then available. He repeated some of the work previously reported, but none of the results were helpful.

On the basis of the foregoing work the chemical information concerning quassin may be summarized as follows: (1) it is an extremely bitter, neutral substance or mixture of substances composed of carbon, hydrogen and oxygen, which contains methoxyl groups; (2) it is not a glucoside; and (3) in general, derivatives are not easily obtained from it.

The work to be reported here is concerned with (1) a practical method for the preparation of quassin, (2) the purification of the crude product, which has been shown to be essentially a mixture of two isomers, and (3) the determination of the molecular formula of these materials.

Of the two main fractions, the one corresponding to Christensen's quassin has been further studied, and some derivatives of it have been prepared and their properties recorded. The information thus obtained is as follows: crude quassin consists essentially of two isomeric compounds having the formula $C_{22}H_{30}O_6$. One melts at 205–206° and is undoubtedly the material studied by Christensen. The other isomer melts at 225–226° and has properties other than its melting point which distinguish it from the first. It is proposed to retain the name "quassin" for the first isomer and call the second "neoquassin." Both compounds have two methoxyl groups.

When treated with boiling 3.5% hydrochloric acid, quassin loses one methoxyl group and yields a compound, $C_{21}H_{28}O_6$, which is insoluble in carbonates and bicarbonates but is freely soluble in alkali hydroxides and in many organic solvents. If, however, constant-boiling hydrochloric or hydrobromic acid is used, the quassin loses two methoxyl groups and two hydrogen atoms and yields a compound, $C_{2}H_{24}O_6$, which is freely soluble in alkalies but relatively insoluble in methanol or ethanol. This material melts at 263° with decomposition. Doubtless the substance is that called quasside or quassic acid by earlier workers. It is proposed to designate this compound as "quassinol." Acetylation of quassinol yields a monoacetyl derivative.

The action of acetic anhydride and sodium acetate upon quassin itself produces at least three substances. One is an anhydro compound, $C_{22}H_{28}O_5$, m. p. 196°, which represents a loss of a molecule of water from quassin; the second is a dehydro compound, $C_{22}H_{28}O_6$, m. p. 256°, containing two less hydrogen atoms than the starting material; and the third is an isomer of quassin, m. p. 214–215°, which is identical with a substance that has been isolated from the wood of *Picraena excelsa*. This is probably one of the picrasmins reported by Massute.[6] Work upon this phase of the problem is in progress and will be reported separately.

The action of chromic acid upon quassin is unusual. When an acetic acid solution of sodium dichromate is allowed to act upon quassin, a slow reaction occurs, and at the end of a week the dichromate is completely reduced. From this mixture is obtained about a 50% yield of a white crystalline material, m. p. 221°, which is isomeric with the starting material.

Attempts to obtain the material by allowing an acetic acid solution of quassin to stand, as in the chromic acid experiment, failed, and only the original material was obtained.

The reactions that have been discussed are represented diagrammatically in the accompanying chart.

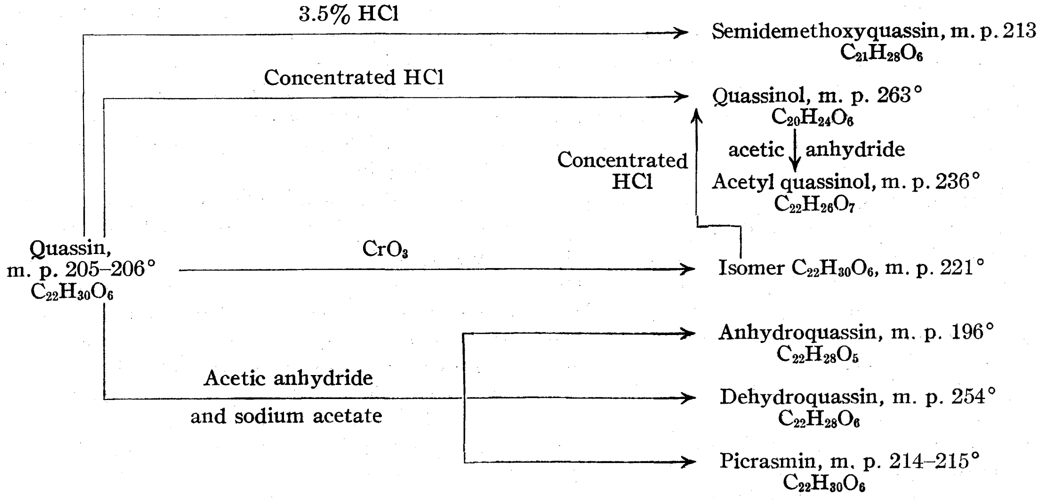
Experimental

Preparation of Quassin.—Quassia chips (20 kg.) were extracted by allowing them to stand in hot water for three hours. The decoction was decanted, and the process was repeated three times. Approximately 70 liters of extract was obtained from each treatment. Each extract was treated with a solution of normal lead acetate until further addition failed to give a precipitate; then, without removal of the separated material, sufficient activated carbon (Carbex) was added to adsorb the quassin. Complete adsorption was determined by the absence of a bitter taste in a filtered test portion.

The quantities of lead acetate and carbon necessary for each of the four extracts were

Extract no.	Carbon, g.	Lead acetate, g.
1	600	150
2	400	100
3	200	50
4	150	50

Reactions of quassin upon which a report has been made



The carbon was removed from each of the extracts and air-dried. It was then mixed, divided into two portions, and each portion was thoroughly percolated with chloroform. Each chloroform extract (representing 10 kg. of quassia chips) was concentrated to dryness under reduced pressure and then dissolved in 150 cc. of methanol. To this solution 950 cc. of hot water (*ca.* 60°) was added, and the turbid liquid was filtered through a thin layer of norit on a Büchner funnel.

Crystallization of crude quassin usually began at once and was completed within two days. Upon concentration, the mother liquors from the crystals gave an additional quantity of crystals. The yield from a number of experiments ranged from 0.15 to 0.18% with an average of 0.16%.

The crude material consisted principally of two isomeric compounds. One was in the form of thin, colorless plates which melted at 205–206°. The other separated from dilute methanol as dense, colorless prisms with a melting point of 225–226°.

The separation of these two isomers was accomplished in essentially the following manner.

One gram of the crude material was dissolved in 10 cc. of boiling methanol and diluted with an equal volume of hot water. The solution was then filtered through a thin layer of norit and allowed to crystallize. The substance obtained, which was approximately 50% of the starting material, consisted largely of quassin (m. p. 205–206°), with some neoquassin. The mother liquors were heated to dissolve any crystalline material, two volumes of water were added and this solution was allowed to crystallize. The crystals, which began to sinter at 205° but did not melt clear until 222°, were mainly neoquassin.

The mother liquors were then concentrated under reduced pressure, and the separated materials were removed from time to time. These fractions were shown by microscopic examination and melting point determinations to consist of both substances, but one or the other usually predominated. The fractions that consisted dominantly of quassin were combined, and the dominantly neoquassin fractions were united. Each was then dissolved in hot methanol and recrystallized by adding two volumes of water. The mother liquors were concentrated as outlined above, and the process was repeated until quassin and neoquassin with sharp melting points and uniform crystalline habit were obtained. The proportion of quassin to neoquassin was estimated to be approximately 2 to 1.

Small quantities of lower and higher melting products were also obtained, but as difficulty was experienced in purifying them, their analysis will be reserved until sufficient material is accumulated to make their characterization certain.

Quassin.—Quassin separates from dilute methanol as thin, colorless rods and micaceous plates which melt at 205–206°. In parallel polarized light (crossed nicols) the rods have straight extinction and positive elongation. In convergent polarized light (crossed nicols) the plates invariably extinguish sharply, indicating that η_β is more or less perpendicular to the broad base, precluding interference figures. The indices of refraction of the material are η_α 1.575; η_γ 1.590.[7]

A solution of 122.8 mg. of quassin in 2.28 cc. of chloroform (*C*, 5.38), when placed in a 96-mm. tube at 20°, rotated the plane of polarized light 2.06° to the right. Therefore, $[\alpha]^{20}\text{D}$ is +39.8°. This value and those to be given subsequently were all obtained with small quantities and microapparatus. They are therefore given, not as precision measurements, but rather to indicate their order of magnitude. A duplication determination with the above sample gave a value of $[\alpha]^{20}\text{D}$ +41°. Active hydrogen determined by the Tschugaeff–Zerewitinoff method gave a value equivalent to one atom.

Anal. Calcd. for $C_{22}H_{30}O_6$: C, 67.67; H, 7.75; OCH_3 (2), 15.9; mol. wt., 390.3; active H (1), 0.26. Found: C, 67.7, 67.8; H, 7.74, 7.73; OCH_3, 15.84; mol. wt. (Rast), 399; active H, 0.28.

Neoquassin.—Neoquassin separates from dilute methanol as dense, colorless six-sided prisms and quadrilateral plates which melt at 225–226°. $[\alpha]^{20}\text{D}$ is +46.6°; *C*, 4.92 in chloroform solution. In parallel polarized light

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[7] The optical crystallographic data reported here were determined by George L. Keenan, of the Food and Drug Administration, U. S. Department of Agriculture. The values of the refractive indices are all ±0.003.

(crossed nicols) many fragments remain bright upon rotation of the microscope stage, while others extinguish sharply. In convergent polarized light (crossed nicols) partial biaxial interference figures are common. The refractive indices are η_α 1.575; η_β 1.600; η_γ 1.626.

Anal. Calcd. for $C_{22}H_{30}O_6$: C, 67.67; H, 7.75; OCH_3 (2), 15.9; mol. wt., 390.3. Found: C, 67.8; H, 7.8; OCH_3, 15.5; mol. wt. (Rast), 387.

Semidemethoxyquassin.—A suspension of 1 g. of quassin in 20 cc. of 10% hydrochloric acid and 40 cc. of water was boiled one and a half hours. After the resulting solution cooled somewhat, it was treated with potassium hydroxide until it remained just acid to Congo red. After three days approximately 0.6 g. of crystalline material had separated. This was dissolved in ethyl acetate, filtered, concentrated to a small volume and allowed to crystallize. A poor yield (160 mg.) of dense colorless prisms, tending to be six-sided, which began to sinter at 195° and flowed at 209–211°, was obtained. A second recrystallization from ethyl acetate brought the material to a constant melting point of 213°.

In parallel polarized light (crossed nicols) the extinction is straight and the elongation negative. No interference figures were observable in convergent polarized light (crossed nicols). The refractive indices of the crystals are η_α 1.517 (common lengthwise); η_β 1.585; η_γ 1.613.

Anal. Calcd. for $C_{21}H_{28}O_6$: C, 67.0; H, 7.5; OCH_3 (1), 8.25. Found: C, 67.1; H, 7.6; OCH_3, 8.2.

The crystals obtained from ethyl acetate may be recrystallized conveniently by dissolving them in water made slightly alkaline with potassium hydroxide and then acidifying the solution with hydrochloric acid. The resulting crystals, after thorough drying, begin to sinter at 195° and flow at 207°. This material gave the following analysis: C, 67.0; H, 7.6; OCH_3, 8.2.

Quassinol.—The action of constant-boiling hydrobromic or hydrochloric acid upon quassin yields quassinol, but the procedure that gave the best yields and the cleanest product is as follows. One gram of quassin dissolved in a solution of 10 cc. of acetic acid and 3 cc. of concentrated hydrochloric acid was heated in a boiling water-bath for one and one-half hours. The dark solution was diluted with four volumes of water, and the hydrochloric acid was neutralized with the calculated quantity of potassium hydroxide. The liquid was cooled with ice and allowed to crystallize. The mother liquors from the crystals were evaporated to dryness under reduced pressure, the salt was dissolved in water and the resulting mixture extracted with chloroform. The extract was dried, concentrated to a sirup and treated with a little hot methanol. Crystallization began at once. The crystalline material filtered from the original aqueous acetic acid reaction mixture was digested with hot methanol, and the resulting quassinol was added to that obtained from the chloroform extract of the mother liquors. In all 1 g. of quassin yielded 0.3 g. of quassinol, m. p. 262°. It was recrystallized by dissolving in boiling chloroform, filtering its solution through norit, concentrating the filtrate until crystallization began and then adding about five volumes of methanol. Thus obtained, it consisted of colorless rods which melted at 263° with decomposition. A solution of 114.9 mg. in 10 cc. of chloroform and observed in a 2-dm. tube at 20° rotated the plane of polarized light 1.44° to the right $[\alpha]^{20}D$ is therefore +62.6°. In parallel polarized light (crossed nicols) the extinction is straight and the elongation is positive. In convergent polarized light (crossed nicols) only faint biaxial interference figures characteristic of sections perpendicular to the acute bisectrix, are shown: η_α 1.518 (crosswise); η_β 1.543 (crosswise); η_γ >1.733 (lengthwise).

Anal. Calcd. for $C_{20}H_{24}O_6$: C, 66.6; H, 6.7; mol. wt., 360.3. Found: C, 66.8; H, 6.8; mol. wt. (Rast), 373.

Acetylquassinol.—A solution of 300 mg. of quassinol in 3 cc. of pyridine and 1.5 cc. of acetic anhydride was allowed to stand overnight. Upon dilution of the mixture with water, 300 mg. of crystalline material, m. p. 232°, separated. It was recrystallized from boiling 95% ethanol. The yield was 240 mg. and its melting point was 236° with evolution of gas.

Anal. Calcd. for $C_{22}H_{26}O_7$: C, 65.6; H, 6.5; acetyl (1), 10.7; mol. wt., 402.3. Found: C, 65.6; H, 6.6; acetyl, 11.2; mol. wt. (Rast), 422.

Action of Acetic Anhydride and Sodium Acetate upon Quassin.—One gram of quassin, 0.25 g. of dry sodium acetate, and 8 cc. of acetic anhydride were refluxed for one and one-half hours. The greater part of the acetic anhydride was then removed by distillation, and about 35 cc. of water was added to the mixture. Upon being stirred, the reaction product gradually crystallized, yielding 0.8 g. of material which melted between 160–170°. This was dissolved in hot methanol and an equal volume of water added. Crystallization began at once and yielded 390 mg. of a substance which melted at 190°. A second recrystallization in the same manner sufficed to yield a pure product, m. p. 196°. This was an anhydroquassin formed by the elimination of 1 mole of water from a mole of quassin.

Anal. Calcd. for $C_{22}H_{28}O_5$: C, 70.9; H, 7.6; OCH_3 (2), 16.7. Found: C, 70.7; H, 7.6; OCH_3, 16.8.

The mother liquor from the first recrystallization of the crude acetylation product was diluted with three volumes of water and allowed to crystallize for a day. A small quantity of material which melted unsharply at about 235° was obtained. This was twice recrystallized from its solution in acetic anhydride by adding three volumes of *n*-butyl ether. Thus obtained, the material was pure and separated as boat-shaped crystals tending to be long hexagonal plates. Its melting point was 254°. Analysis indicated it to be a dehydroquassin.

Anal. Calcd. for $C_{22}H_{28}O_6$: C, 68.0; H, 7.3; OCH_3 (2), 16.0; mol. wt., 388.3. Found: C, 67.6; H, 7.4; OCH_3, 15.6; mol. wt. (Rast), 403.

The mother liquors from the dehydro compound were concentrated under reduced pressure to a small volume, which caused a crystalline material to separate. Its melting point was 205–210°. Upon recrystallization from 25% methanol, it consisted of long rectangular plates melting at 214°. When mixed with picrasmin, m. p. 215–216°, there was no depression of the melting point.

Anal. Calcd. for $C_{22}H_{30}O_6$: C, 67.67; H, 7.75; OCH_3 (2), 15.9. Found: C, 67.5; H, 7.7; OCH_3, 15.9.

Action of Chromic Acid upon Quassin.—Ten cubic centimeters of a 10% acetic acid solution of crystalline sodium dichromate was added to a solution of 1 g. of quassin in 5 cc. of hot acetic acid. After a week two volumes of water was added to the solution and the mixture was concentrated under reduced pressure almost to dryness. Water was then added and the resulting crystals were collected. The yield was 0.5 g. and the material melted at 217°. One recrystallization from dilute methanol gave a pure product, m. p. 221°. It consisted of colorless rectangular rods and plates, which had optical crystallographic properties very similar to the starting material. In parallel polarized light (crossed nicols) the extinction is straight and the elongation is positive. Most of the crystals extinguish sharply (crossed nicols), although plates occasionally extinguish in a hazy, indefinite manner. In convergent polarized light (crossed nicols) these plates show a dim biaxial interference figure with both of the isogyres in the field (section perpendicular to the acute bisectrix). Owing to the dimness of the figure, the magnitude of the axial angle could not be determined definitely, but it appeared to be small. The refractive indices are: η_α 1.575 (common crosswise); η_γ 1.585 (common lengthwise); η_β could not be determined with certainty. Its specific rotation in chloroform solution (C, 5.22) was found to be $[\alpha]^{20}\text{D}$ +35.1°.

Anal. Calcd. for $C_{22}H_{30}O_6$: C, 67.67; H, 7.75; OCH_3 (2), 15.9. Found: C, 67.8; H, 7.4; OCH_3, 15.9.

Treatment of this material with acetic and hydrochloric acids as outlined for the preparation of quassinol gave just twice the yield of quassinol that was obtained from quassin itself. The identity of the quassinol was proved by its melting point, mixed melting point and optical properties.

Summary

A convenient method has been developed for the preparation of crude quassin. This material has been shown to consist essentially of two isomeric substances of the formula $C_{22}H_{30}O_6$, each containing two methoxyl groups. These have been separated, and directions are recorded for doing this. It is proposed to retain the name "quassin" for the isomer melting at 205–206° and designate the other isomer, m. p. 225–226°, as "neoquassin." A summary of the relationships between quassin and several derivatives is shown diagrammatically.

Washington, D. C. Received March 18, 1937

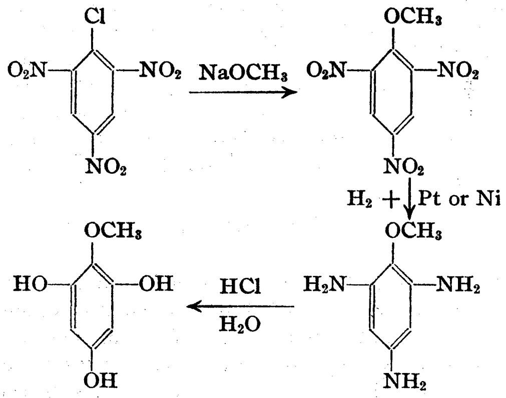
[Contribution from the Chemical Laboratory of the University of Illinois]

A Synthesis of Iretol

By R. E. Damschroder and R. L. Shriner

Iretol was first isolated by de Laire and Tiemann[1] as a degradation product of a glucoside obtained from *Iris florentina*. It is produced by alkaline degradation of tectorigenin[2] and of wogonin.[3] The structure of iretol as 2,4,6-trihydroxyanisole was established by conversion to phloroglucinol by de Laire and Tiemann,[1] and by a synthesis by Kohner,[4] who reduced 2,4,6-trinitroanisole with tin and hydrochloric acid to a diaminohydroxyanisole, which was then hydrolyzed to iretol. When this method was used for the preparation of iretol, it was found that the yields were very low, and that the presence of the large amounts of tin salts at the last step rendered the isolation of the product very difficult. Any procedures used for the preparation of this polyhydroxybenzene must be simple and require as short a time as possible, because aqueous solutions of the intermediate amino compound, as well as the final product, are very sensitive to oxygen of the air, and readily undergo oxidation to highly colored compounds.

A modified synthesis has been developed, using the reactions



The catalytic reduction of 2,4,6-trinitroanisole must be carried out rapidly, using a very active catalyst. A high ratio of catalyst to compound must be used. Yields of the 2,4,6-triaminoanisole as high as 81% were obtained, provided the product was isolated with the exclusion of oxygen. The final hydrolysis was accomplished with hydrochloric acid alone, no stannous chloride being necessary. Isolation of the iretol must be accomplished in a carbon

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(1) De Laire and Tiemann, *Ber.*, **26**, 2015 (1893).

(2) Shibata, *J. Pharm. Soc. Japan*, **543**, 380 (1927).

(3) Hattori and Hayashi, *Ber.*, **66B**, 1279–1280 (1933).

(4) Kohner, *Monatsh.*, **20**, 933 (1899).

dioxide atmosphere, the final purification by a vacuum sublimation. The yields varied from 40 to 75%.

Experimental Part

Picryl Chloride.—Nitration of 2,4-dinitrochlorobenzene according to the directions of Frankland and Garner[5] gave 80% yields of picryl chloride, melting at 79–82°.

2,4,6-Trinitroanisole.—A solution of 50 g. of picryl chloride in 300 cc. of hot methanol is added slowly, with stirring, to a cold solution of sodium methoxide prepared by adding 13 g. of sodium to 200 cc. of methanol. The deep red solution is cooled in an ice-bath for two hours, and the red crystalline precipitate removed by filtration. This precipitate, a double compound of 2,4,6-trinitroanisole and sodium methoxide,[6] is suspended in 500 cc. of water, and the mixture made distinctly acid with concentrated hydrochloric acid. The mixture is filtered, and the precipitate dissolved in hot methanol. Rapid cooling of this solution gave an 82% yield of yellow prisms, which melted at 58–59°.

2,4,6-Trinitroanisole is peculiar in that it exists in several crystalline forms which melt at different temperatures. By very slow crystallization of the compound from dilute methanol solutions, four distinct types of crystals were obtained.

Crystal form	M. p., °C.
Square plates	50–51
Hexagonal plates	56–57
Prisms	58–59
Needles	68–69

The needles melting at 68–69° correspond to the form described by Meisenheimer,[7] but other investigators[6,8] have obtained forms melting from 58 to 65°.

The lower-melting forms, after standing in stoppered tubes for four months, melted at 68°, indicating that this form is the stable one, and that a gradual transition to the higher-melting form had occurred. In fact, once the higher-melting form had been obtained, it was then impossible again to secure crystals of the three lower-melting forms. The compound was analyzed to check its composition.

Anal. Calcd. for $C_7H_5O_7N_3$: N, 17.28. Found: N, 17.37.

2,4,6-Triaminoanisole.—A solution of 7.5 g. of 2,4,6-trinitroanisole in 170 cc. of absolute ethanol was reduced with hydrogen at a pressure of 2 to 3 atmospheres in the presence of a catalyst. If platinum oxide (0.2 g.) is used as the catalyst,[9] it is important that the catalyst be active enough to cause complete reduction in ten minutes or less. An 80% yield of the triamine may then be obtained. The cause of variations in activity of the catalyst appeared to be associated with the quality of platinum chloride. Catalyst prepared from platinum chloride, purified by precipitation as ammonium chloroplatinate, gave excellent results, as did chloroplatinic acid purchased from Mallinckrodt Chemical Works. With inactive catalysts, the yield of amine drops markedly. One batch of catalyst, prepared from a commercial platinum chloride, required two hours for absorption of the theoretical amount of hydrogen. Only highly colored condensation products were formed, and no triamine could be isolated.

Raney nickel[10] also was found to be a very effective catalyst, provided a 1:1 ratio of catalyst to compound was used, so that the reduction was completed in fifteen to thirty minutes. The yield of amine using this catalyst ranged from 68 to 78%. The results were more consistent with different batches of catalyst than was the case with platinum.

This reduction of the trinitro compound is exothermic and because of the rapid rate of reduction which is necessary, the container heats up considerably. It is desirable to place a safety glass shield between the operator and the reduction apparatus.

After the theoretical amount of hydrogen had been absorbed, the reduction mixture was filtered quickly, and the solvent removed with a water pump, at the same time passing in a slow current of carbon dioxide through the solution. The triamine started to precipitate when the volume reached about 20 cc. The mixture was then cooled in an ice-bath, and the product removed by filtration and washed with small amounts of cold absolute ethanol. The crude product varies from a light tan to a dark brown in color, and melts at 105 to 110°. It is purified by recrystallization from hot absolute ethanol with the aid of norite. The pure compound melted at 116.5–117.5° (corr.).

Anal. Calcd. for $C_7H_{11}ON_3$: N, 27.44; methoxyl, 20.26. Found: N, 27.42; methoxyl (Zeisel), 20.80.

2,4,6-Trihydroxyanisole (Iretol).—A solution of 6.12 g. of the crude triaminoanisole in 280 cc. of air-free water containing 9 cc. of concentrated hydrochloric acid was refluxed for twenty hours in an atmosphere of carbon dioxide. The brown solution was cooled, and a slight amount of brown, insoluble material removed by filtration. The water was removed by vacuum distillation, passing a stream of carbon dioxide through the capillary. The solution has a tendency to foam, and must be carefully watched. Bumping occurs near the end of the distillation, due to the precipitation of ammonium chloride. The dry residue is then thoroughly extracted with two 350-cc. portions and one 150-cc. portion of ether. The residue should be entirely free of any oily matter.

The combined ether extracts are dried over magnesium sulfate for one hour, and the ether is then removed by distillation.

If the triaminoanisole was exceptionally pure, the iretol may crystallize as the ether is removed. If the product is oily, it can be caused to solidify by adding a few cubic centimeters of dry ether and warming on a steam-bath for several minutes. The crude iretol is extracted with a small amount of dry ether and dried by warming for thirty minutes on a steam-bath in a carbon dioxide atmosphere. The crude product is tan colored, and melts at 165–175°. The iretol is most easily purified by sublimation at 150–

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(5) Frankland and Garner, *J. Soc. Chem. Ind.*, **39**, 259T (1920).

(6) Jackson and Boos, *Am. Chem. J.*, **20**, 447 (1898).

(7) Meisenheimer, *Ann.*, **323**, 242 (1902).

(8) Cahours, *ibid.*, **69**, 238 (1849); Post and Mehrtens, *Ber.*, **8**, 1552 (1875); Hantzsch, *ibid.*, **39**, 1097 (1906).

(9) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 452.

(10) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

160° under 2 mm. pressure against a tube cooled with acetone and dry ice. Clear, feathery needles were obtained which melted at 187.5–188.5° (corr.). The poorest yield of sublimed iretol was 40%, and the best was 75% of the theoretical amount.

Anal. Calcd. for $C_7H_8O_4$: C, 53.83; H, 5.17; methoxyl, 19.87. Found: C, 54.10; H, 5.38; methoxyl (Zeisel), 19.60.

Iretol is stable when pure and dry, but readily turns dark if exposed to moisture and oxygen.

Summary

2,4,6-Trinitroanisole may be satisfactorily reduced catalytically to give 68 to 81% yields of 2,4,6-triaminoanisole, provided the reduction is carried out rapidly. The triamine may be hydrolyzed to 2,4,6-trihydroxyanisole (iretol) in 40 to 75% yields by means of hydrochloric acid.

URBANA, ILL. RECEIVED MARCH 22, 1937

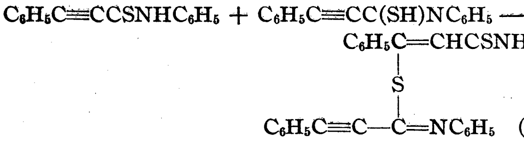
[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY, TUFTS COLLEGE]

The Action of Hydroxylamine and Hydrazine on Acetylenic Thioamides

BY DAVID E. WORRALL

It has been shown previously that sodium phenylacetylene forms addition products with aromatic isothiocyanates.[1] Since the resulting thioamides contain an acetylenic group, they behave in a characteristic manner with certain reagents. These reactions have been investigated in the present communication.

Phenylpropiol thioanilide[1] obtained from phenyl isothiocyanate is destroyed easily by heat or acids; consequently the addition of water to the acetylenic group is yet to be observed. Like any thioamide it is soluble in aqueous alkali. On warming it polymerizes, a change that has been assumed to result from the interaction of I with its enol

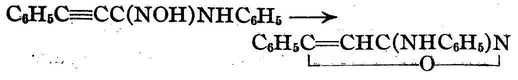


$$C_6H_5C{\equiv}CCSNHC_6H_5 + C_6H_5C{\equiv}CC(SH)NC_6H_5 \longrightarrow \begin{array}{l} C_6H_5C{=}CHCSNHC_6H_5 \\ \quad | \\ \quad S \\ \quad | \\ C_6H_5C{\equiv}C{-}C{=}NC_6H_5 \end{array}$$

(II)

The product is a highly colored dimer, still soluble in alkali, which reacts with hydroxylamine through hydrogen sulfide elimination. With bromine, part of the molecule is converted into the dibromide of I. The other portion changes into an intractable tar, precisely the effect of bromine on I, accompanied by the formation of hydrogen bromide.

I also reacts in a characteristic manner with hydroxylamine, the first formed oxime rearranging into an isoxazole.



$$C_6H_5C{\equiv}CC(NOH)NHC_6H_5 \longrightarrow \underbrace{C_6H_5C{=}CHC(NHC_6H_5)N}_{O}$$

(III)

III reacts smoothly with nitric acid and with bromine, forming products in which substitution has taken place in the aniline group, evidenced by the production of benzoic acid on oxidation. In a similar manner hydrazine and phenylhydrazine lead to substituted pyrazoles. The pyrazole obtained from hydrazine is of such a nature that the aniline group present is capable of reacting with three equivalents of bromine or nitric acid.

A small amount of by-product is usually present in the preparation of III, the analysis of which indicates that the original substance has taken on one equivalent of oxygen. Since the aromatic thioamides are readily converted into thiazoles under mild oxidizing conditions, the substance[2] may be regarded as phenacyl benzothiazole, $C_6H_5COCH_2\underbrace{C{=}NC_6H_4}_{S}$. It results perhaps from the addition of hydroxylamine to the acetylenic group followed by oxidation and hydrolysis under the influence of the organic base.

Experimental

Phenylpropiol Thioanilide.—To 0.5 gram mole of phenylacetylene converted into the sodium derivative and suspended in dry ether was added the equivalent of phenyl isothiocyanate. The bulky product after several hours was filtered and washed with ether. The residue was decomposed immediately in small lots (unchanged sodium present) with a well-stirred mixture of ice and water. An excess of dilute acid was used to complete the reaction after which the product, following thorough washing with dilute alcohol, was suspended in chloroform. Petroleum ether in excess was then added; final yield 70 g. Because of destructive decomposition, heating must be avoided. It separated from warm chloroform–petroleum ether mixtures as tiny yellow needles, decomposing at 113–114°. *Anal.* Calcd. for $C_{15}H_{11}NS$: C, 75.9; H, 4.6; S, 13.5. Found: C, 75.5; H, 4.6; S, 13.7. It changes into a glossy black resin if heated to 100° for a few minutes. The thio-

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(1) Worrall, THIS JOURNAL, **39**, 697 (1917).

(2) Jacobsen, *Ber.*, **21**, 2629 (1888).

anilide is soluble in aqueous alkali, precipitating out unchanged on neutralization with acid, but polymerizing on the application of heat. A similar change takes place more slowly on heating an alcoholic solution of the substance in the absence of alkali accompanied by considerable decomposition into hydrogen sulfide and an intractable black tar. Destructive decomposition occurs slowly at room temperature if an acid is added to the alcoholic solution. All attempts to obtain a ketone by hydration of the acetylenic group failed. Mercuric salts decompose the substance. Bromine reacts instantly with blackening of the solution and subsequent elimination of hydrogen bromide fumes. An odor similar to sulfur chloride was noticed in the tarry residue.

Bis-phenylpropiolthioanilide was obtained by heating I with alcohol under a reflux condenser for several hours. The lustrous bronze colored plates produced were filtered while hot and thoroughly washed with warm alcohol; yield approximately 40%. *Anal.* Calcd. for $(C_{15}H_{11}NS)_2$: C, 75.9; H, 4.6. Found: C, 75.8; H, 4.6. A molecular weight determination using bromoform as a solvent indicated a dimer. It sinters at about 250°, decomposing indefinitely. Hydrogen sulfide was eliminated slowly by the action of hydroxylamine. The tarry residue on examination was found to contain sulfur, although no definite substance was isolated.

Phenylpropiolthioanilide Dibromide.—An equal weight of bromine mixed with II suspended in chloroform caused crystal formation in a few minutes. On standing, copious evolution of hydrogen bromide fumes occurred, but the amount of solid material did not change noticeably. Most of the products of the reaction remained in solution and were discarded, as tars separated on evaporation. The crystalline material separated from a large volume of glacial acetic acid in small yellow plates, decomposing at 226–227°. *Anal.*[3] Calcd. for $C_{15}H_{11}NSBr_2$: C, 45.3; H, 2.8; Br, 40.3. Found: C, 45.5; H, 2.7; Br, 40.2.

3-Anilino-5-phenylisoxazole.—An alcohol solution containing three equivalents of hydroxylamine was mixed with 10 g. of I and slowly heated to the boiling point. Heating was continued under a reflux condenser until no further hydrogen sulfide evolution occurred. The red solution, filtered if necessary, was poured into water. The product was crystallized repeatedly from alcohol to remove colored impurities, finally separating as sparkling plates, m. p. 142–143°; yield approx. 2 g. *Anal.* Calcd. for $C_{15}H_{12}ON_2$: C, 76.2; H, 5.1. Found: C, 76.1; H, 5.2. It is unchanged after long heating with either acid or alkali, but readily reduces permanganate solutions.

I-Phenacyl Benzothiazole.—A substance insoluble in alcohol was obtained with the isoxazole if concentrated solutions were used; yield 0.4 g. It was crystallized from glacial acetic acid in the form of deep yellow needles decomposing at 190–191°. *Anal.* Calcd. for $C_{15}H_{11}ONS$: C, 71.1; H, 4.3; S, 12.6. Found: C, 70.8; H, 4.4; S, 12.5. It is soluble in alcoholic potash, from which it is precipitated unchanged by acid or dilution with water. Hot alcoholic potash decomposes it into a tar. A small amount of an oil soluble in acid and with a pyridine-like odor was obtained on long heating with hydrochloric acid.

3-*p*-Bromoanilino-5-phenylisoxazole.—The isoxazole was brominated in chloroform and crystallized from alcohol, separating as plates, m. p. 158°. *Anal.* Calcd. for $C_{15}H_{11}ON_2Br$: Br, 25.4. Found: Br, 25.5. On oxidation with permanganate, benzoic acid was isolated from the material insoluble in acetone.

3-[2,4-Dinitroanilino]-5-phenylisoxazole.—The isoxazole dissolved readily in concd. nitric acid. Water throws out of solution the product which separated from glacial acetic acid as glittering yellow plates, m. p. 245–246°. *Anal.* Calcd. for $C_{15}H_9O_5N_4$: C, 55.5; H, 2.8. Found: C, 55.9; H, 2.8.

3-Anilino-5-phenylpyrazole.—I (10 g.) was heated with two equivalents of hydrazine, the excess being necessary to avoid the formation of II. Nearly colorless needles, m. p. 151–152°, were obtained eventually by repeated crystallization of the crude product; yield 3–4 g. The hydrochloric acid salt, prepared by adding a few drops of concd. acid to the alcohol solution, m. p. 166–167°, was used for analysis. *Anal.* Calcd. for $C_{15}H_{13}N_3 \cdot HCl$: C, 66.3; H, 5.2. Found: C, 66.5; H, 5.2. The base is sparingly soluble in hot water and unaffected by hot acid or alkali.

3-[2,4,6-Tribromoanilino]-5-phenylpyrazole.—The tribromo derivative, obtained as before, separated as a salt that hydrolyzed in the presence of alcohol or water. It was crystallized from a large volume of alcohol, forming needles decomposing at 206–207°. *Anal.* Calcd. for $C_{15}H_{10}N_3Br_3$: C, 38.1; H, 2.1. Found: C, 38.4; H, 2.3. On extraction with hot water of the acetone-insoluble material obtained by oxidation with permanganate, two products were found, benzoic acid and a yellow bromine-containing substance that was not examined further.

3-[2,4,6-Trinitroanilino]-5-phenylpyrazole.—Nitric acid dissolved the pyrazole, yielding a product that was crystallized from glacial acetic acid. It forms lustrous yellow needles decomposing at 266°. *Anal.* Calcd. for $C_{15}H_{10}N_6O_6$: C, 48.6; H, 2.7. Found: C, 48.3; H, 3.1.

1-Phenyl-3-anilino-5-phenylpyrazole.—Obtained from two equivalents of phenylhydrazine with 10 g. of I as pointed prisms, m. p. 153–154°, yield 4 g. *Anal.* Calcd. for $C_{21}H_{17}N_3$: C, 81.0; H, 5.5. Found: C, 81.4; H, 5.4. The dibromo derivative, needles, m. p. 181°, and the trinitro, tiny yellow plates, m. p. 197–198°, were prepared and analyzed.

Summary

Phenyl isothiocyanate forms an unsaturated thioanilide with phenylacetylene, a substance easily destroyed by acids, free halogens or heat. It is polymerized by alkali and reacts with hydroxylamine, hydrazine and phenylhydrazine, forming heterocyclic compounds from which bromo and nitro derivatives have been prepared.

MEDFORD, MASS.

RECEIVED MARCH 5, 1937

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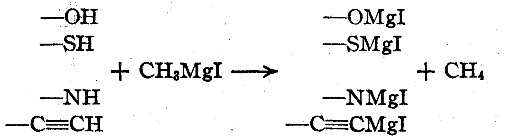
(3) Low results occur in determination of bromine by the Carius method unless precautions are taken, as nitric acid promptly liberates hydrogen bromide from the substance.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Compounds. XVI. Detection of the —SH Group

BY HENRY GILMAN AND JOSEPH F. NELSON

The Tschugaeff–Zerewitinoff[1] analysis makes it possible to determine, qualitatively and quantitatively, active or acidic hydrogens by measurement of the volume of methane evolved when a weighed amount of sample is treated with an excess of methylmagnesium iodide.



$$\begin{array}{c} -OH \\ -SH \\ -NH \\ -C{\equiv}CH \end{array} + CH_3MgI \longrightarrow \begin{array}{c} -OMgI \\ -SMgI \\ -NMgI \\ -C{\equiv}CMgI \end{array} + CH_4$$

A study of other organometallic compounds indicates that it may be possible, by use of appropriate organometallic compounds, to effect selective or preferential reactions with specific active hydrogen types. We are reporting at this time the use of triethylbismuth and tetraethyllead for detecting the —SH group.

Experimental Part

Materials.—A convenient method for the preparation of triethylbismuth is one patterned after the procedure of Schaefer and Hein[2] for the preparation of trimethylbismuth. To an ethylmagnesium bromide solution prepared from 1.4 moles of ethyl bromide in 400 cc. of ether, was added slowly and with rapid stirring 200 g. of an ether solution containing 0.4 mole of bismuth chloride. Because of the inflammability of triethylbismuth all operations were carried out in a nitrogen atmosphere. Heat was applied until the reaction was complete, and a large quantity of gray precipitate formed.

Most of the ether was then removed by fractionation through an efficient column, a hot water-bath being used. Triethylbismuth, like some other organometallic compounds, undergoes a ready ether distillation, and a fractionating column reduces the carry-over of triethylbismuth. The remaining ether and triethylbismuth were then distilled off at 4 mm. pressure into a 250-cc. modified Claisen flask cooled by an ether–dry ice mixture. In this distillation an oil-bath was used, and the external temperature was raised gradually to 170° near the end of the distillation. Abrupt and excessive heating should be avoided.

The ether was finally distilled from the distillate, and the triethylbismuth then collected at about 123° (150 mm.). The yield was 88%.

The tetraethyllead and the several compounds studied were purified by customary procedures.

Procedure.—The usual Zerewitinoff apparatus and technique were used, 5 cc. of *n*-butyl ether or of 1,4-dioxane being added to the 0.2–0.4 g. sample. After flushing out the side-bulb with nitrogen, 5 cc. of a 25% (by volume) solution of triethylbismuth in *n*-butyl ether was run into the side-bulb through a bent pipet provided with a stopcock. The main bulb was then flushed with nitrogen and attached to the gas buret.[3] The bulb was then immersed for a few minutes in a water-bath kept at 25°, and the system closed to the atmosphere. A water-bath containing boiling water was then applied and the water kept boiling for a definite time (see Table I), after which the contents of the bulb were cooled quickly and the original water-bath applied to bring the temperature to 25°. Temperature, volume and pressure readings were made fifteen minutes after heating was discontinued. Blanks, averaging 0.3 cc., were made, and this volume was deducted from the total volume measured. The same procedure was used in the tetraethyllead studies. All experiments were checked. The results given in Table I are averages, and the numerical values represent the fractional amount of the active hydrogen that reacted in the time given.

Tetraethyllead and Thiophenol.—In order to determine the number of ethyl groups that can be cleaved, 2 g. (0.018 mole) of thiophenol in 5 cc. of *n*-butyl ether was added to 0.629 g. (0.00194 mole) of tetraethyllead in 5 cc. of *n*-butyl ether, and the solution kept at 100° for six hours with occasional shaking. Gas was evolved quite rapidly at first, and of the 132.8 cc. finally collected only about 10 cc. was evolved in the last three hours. In a check experiment, 126.4 cc. of gas was collected, and these two volumes correspond to 3.07 and 3.20 ethyl groups, respectively.

The sulfur containing organometallic products obtained from the several compounds will be reported later.

The gas obtained from tetraethyllead and *p*-thiocresol was analyzed and shown to be ethane.

Discussion of Results

Organometallic compounds of lesser reactivity than the Grignard reagent almost always give low values in active hydrogen analyses. This applies not only to diethylzinc[4] but to organometallic compounds containing cadmium, mercury, boron, aluminum and tin. However, even though the results obtained with the lesser reactive RM types are only partially quantitative, they are of definite diagnostic value. Furthermore, when there is selective substitution of hydrogen by

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(1) Tschugaeff, *Ber.*, **35**, 3912 (1902); Zerewitinoff, *ibid.*, **40**, 2023 (1907); **41**, 2233 (1908); *Z. anal. Chem.*, **50**, 680 (1911). See also Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

(2) Schaefer and Hein, *Z. anorg. Chem.*, **100**, 297 (1917).

(3) All traces of air are not removed by this procedure. As a consequence, the reagent becomes cloudy, but this appears to be without effect on the result. The ready clouding of triethylbismuth by oxygen suggests the use of triethylbismuth as a delicate test for traces of oxygen. Fortunately, for the purposes of such a test, triethylbismuth is unaffected by moisture.

(4) Haurowitz, *Mikrochemie*, **6**, 88 (1929).

TABLE I

TRIETHYLBISMUTH AND TETRAETHYLLEAD WITH SOME ACTIVE HYDROGEN COMPOUNDS

Average active hydrogen based on heating at 100° for various times.

	$(C_2H_5)_3Bi$		$(C_2H_5)_4Pb$		
	30 min.	120 min.	10 min.	30 min.	60 min.
—SH Compounds					
n-Butyl mercaptan	0.54		0.15	0.23	
n-Heptyl mercaptan	.56	0.63	.45	.61	
Benzyl mercaptan	.50		.57	.67	
Thiophenol	.74			.75	0.75
p-Thiocresol	.67		.55	.72	
Thio-β-naphthol	.50		.37	.49	
1-Mercaptobenzothiazole[a]	.44		.06	.16	.27
Thioacetic acid	.59		.49	.57	
—OH compounds					
Water[a]	0.0				0.0
n-Butyl alcohol	.0				.01
Formic acid[b]				0.12	.27
Acetic acid	.02	0.11		.02	.04[e]
Chloroacetic acid	.06	.22		.52	.68
Dichloroacetic acid	.21	.61		.70	.80
Trichloroacetic acid	.42	.74		.72	.76
Butyric acid	.01				.01
Maleic acid[a]	.09[c]			.68	.78
Benzoic acid	.02[d]			.06	.17
Phenol	.01				.01
2,4-Dibromophenol					.02
2,4-Dinitrophenol					.09
2,4,6-Trinitrophenol	.06			.48	.55[a]
p-Hydroxyazobenzene	.0				.0
Vanillin					.0
1,2,3-Trihydroxybenzene[a]					.02
Acetoxime					.0
Acetophenone oxime	.0				
—NH compounds					
Aniline	0.0			0.0	0.0
2-Amino-4-phenylthiazole[a]	.01			.01	.01
Benzamide[a]	.00			.01	.02
Thiourea[a]	.0				.02
s-Diphenylthiourea[a]	.05	.09		.05	.06
Miscellany					
Phenylacetylene	0.0			0.0	0.0
Acetylacetone	.01				
Azobenzene	.0			.01	.01
Nitrobenzene	.0				
1,2-Dinitrobenzene				.0	.0
1,3-Dinitrobenzene	.0				
1,3,5-Trinitrobenzene	.04			.0	.0[f]
Ethyl disulfide					.0

[a] Dioxane was used as a solvent for these compounds. In all other cases, di-*n*-butyl ether was used. [b] An 87–90% solution of formic acid was used. The gas evolved with tetraethyllead was shown to be ethane. Also the gas from trichloroacetic acid and tetraethyllead was practically pure ethane. [c] Heating for sixty minutes gave 0.13 active hydrogen. [d] Heating for sixty minutes gave 0.03 active hydrogen. [e] Heating for one hundred and twenty minutes gave 0.14 active hydrogen. [f] Heating for ninety minutes gave no active hydrogen.

metal it appears reasonable to expect preferential replacement reactions with the intermediate metallic compounds. For example, acylation and alkylation of a compound containing both —SH and —NH groups may be largely confined to the —SH group after the compound is first treated with triethylbismuth or tetraethyllead.

There is a broad correlation between acidities of weakly acid organic compounds and relative reactivities of organometallic compounds. For example, the weakly acidic hydrogen in benzene is replaced by a metal when the highly reactive alkyl-alkali compounds are used, but not when the moderately reactive Grignard reagents are used. The reaction of —SH but not generally of —OH with triethylbismuth or tetraethyllead appears as a particularly striking exception, for some of the —OH compounds (Table I) which do not react are definitely more acidic than the —SH compounds which undergo substitution of hydrogen by metal. Acidities do play some part even in the substitutions considered, and one illustration from the results reported is the increase in rate of reaction observed with acetic and the chloroacetic acids.[5] For example, with triethylbismuth the number of active hydrogens observed after heating at 100° for two hours is: acetic acid, 0.11; chloroacetic acid, 0.22; dichloroacetic acid, 0.61; and trichloroacetic acid, 0.74. Incidental to the reaction of carboxylic acids with tetraethyllead it should be stated that silica gel is an effective catalyst for replacing one ethyl group to give $(C_2H_5)_3PbOCOR$ compounds,[6] and that three ethyl groups may be removed as ethane by the action of acetic acid at high temperature (250–260°).[7] In the Experimental Part we have reported the replacement of more than three ethyl groups from tetraethyllead by heating with thiophenol at 100°. Historically it is interesting to note that long years ago Dünhaupt[8] obtained bismuth sulfide from triethylbismuth and hydrogen sulfide.

Azo and nitro goups interfere with active hydrogen determinations by the Grignard re-

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(5) If acidities play a significant role one might predict that tellurophenol will cleave organotin and possibly organogermanium compounds.

(6) Browne and Reid, THIS JOURNAL, **49**, 830 (1927).

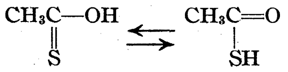
(7) Jones and Werner, *ibid.*, **40**, 1257 (1918).

(8) Dünhaupt, *Ann.*, **92**, 371 (1854).

agent.[9] Triethylbismuth and tetraethyllead, however, do not evolve gas with such groups. The small volume of gas evolved from triethylbismuth and 1,3,5-trinitrobenzene is just about the experimental limit of accuracy.

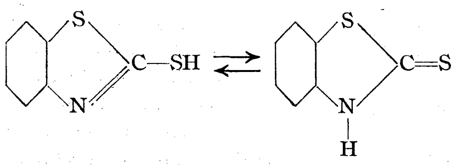
On general grounds triethylbismuth may be preferred to tetraethyllead because it not only gives high values for —SH groups but also is less interfered with by —OH groups. The inflammability and lesser accessibility of triethylbismuth is to be contrasted with the toxicity and accessibility of tetraethyllead.

Some of the results are interesting from the point of view of tautomerism. The replacement of hydrogen by metal noted with thioacetic acid establishes the presence of an —SH group, but throws no light on the equilibrium



$$\underset{\substack{\| \\ S}}{CH_3C}—OH \rightleftarrows \underset{\substack{| \\ SH}}{CH_3C}=O$$

Thioenolization is probably affected by the RM compounds used to establish the presence of active hydrogen groups. What may be a pertinent illustration are the results with 1-mercaptobenzothiazole.



Both triethylbismuth and tetraethyllead show the presence of an —SH group. However, tri-*n*-propylboron which reacts with —SH groups but not with the —NH group, gives no reaction with 1-mercaptobenzothiazole. Slight thioenolization is shown by *s*-diphenylthiourea but not by thiourea.

Some solvents may have special enolizing effects.[10]

Summary

Triethylbismuth and tetraethyllead can be used for the detection of the —SH group. These organometallic compounds do not react with the hydrogens in —NH and —C≡CH groups; they do not react with simple —OH groups, although some strong carboxylic acids undergo generally limited reactions; and there is no interference by azo or nitro groups.

The RM compounds may be useful to establish the existence of thioenolization in compounds like thioacetic acid.

AMES, IOWA RECEIVED FEBRUARY 15, 1937

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[9] Gilman and Fothergill, THIS JOURNAL, **50**, 867 (1928); Gilman, Fothergill and Towne, *ibid.*, **52**, 405 (1930).

[10] Clutterbuck, Raistrick and Reuter, *Biochem. J.*, **29**, 300 (1926).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Passivity of Iron in Chromic Acid Solutions[1]

BY W. H. CONE AND H. V. TARTAR

In a previous paper[2] the authors described some experiments which showed that iron could be made active in chromic acid solutions if a sufficiently reduced pressure were maintained at the time of placing the iron in the solution. Subsequent experiments have shown that this effect of reduced pressure was associated with the presence of some sulfate ion in the solution. Experiments on iron in chromic acid solutions with and without phosphate or sulfate ion under varying conditions of temperature and pressure are described in this paper. Pertinent data on the adsorption of oxygen by iron are also given.

Materials and Apparatus.—Pure chromium trioxide (CrO_3) was prepared from potassium dichromate and sulfuric acid. The crystals were washed with concentrated nitric acid until free of sulfate and then dried at 80° to remove the nitric acid.

The data reported in this paper were obtained using No. 30 iron wire, for standardizing, Fe 99.84%. Some experiments were made with iron of varying purity without any appreciable effect on the results.

Preliminary tests showed that a reduction of pressure after the iron was placed in the chromic acid solution did not produce activity. Consequently in finding the pressure at which the iron became active, it was necessary to use a fresh piece of the metal each time the pressure was changed. To facilitate changing the sample of iron without changing the pressure, a special apparatus was constructed, Fig. 1. When the pressure in the system had been adjusted to the desired value a sample of iron wire was fed from the spool into the electrode vessel by means of the motor-driven feed rolls. The potential of the wire was determined by connecting to a potentiometer through a saturated calomel half cell. A nearly saturated potassium

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[1] Original manuscript received July 27, 1936.

[2] Cone and Tartar, THIS JOURNAL, **56**, 48 (1934).

nitrate solution was used as a bridge to connect the calomel cell with the electrode vessel. After measuring the potential of the iron against the chromic acid solution, the wire was cut and the piece removed by closing the circuit activating the electromagnet. The pressure in the system was then changed and the process repeated until a pressure was found at which there was a sudden change in the potential of the iron.

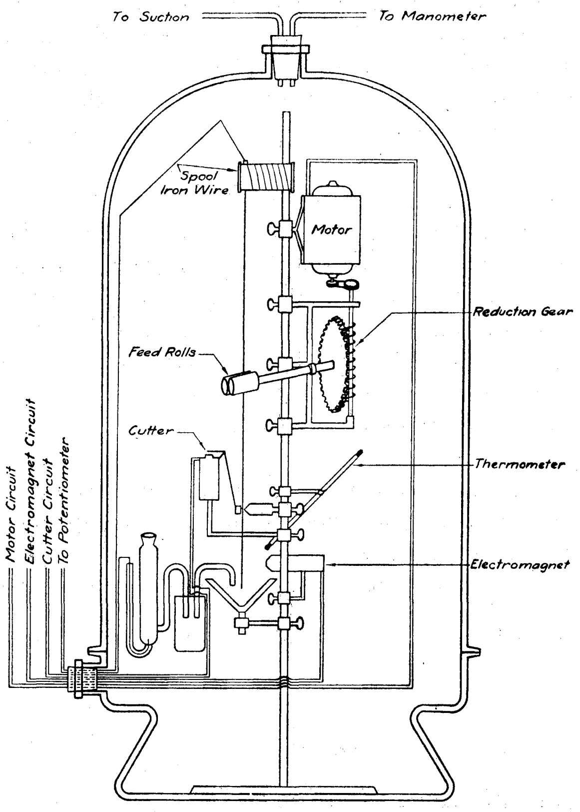

Fig. 1.—Apparatus for studying passivity at reduced pressures.

Experiments with Iron in Chromic Acid Solutions

When iron was placed under reduced pressure and then immersed in a solution of pure chromic acid, of concentrations varying from saturated to quite dilute, it did not become active even when the pressure was reduced to that of the vapor pressure of the solution. Solutions of chromic acid which contained a small amount of sulfuric acid or other activating electrolytes dissolved iron readily if the pressure was sufficiently reduced before placing the iron into the acid. The iron remained passive, however, if introduced into the solution when the pressure was above a given value which is here designated as the transition pressure.

The transition pressures could be determined either by reducing the pressure until the iron was active and then admitting air or oxygen until a sample tested passive or by decreasing the pressure slowly until a sample tested active. The results were the same within 10 mm. Since each test was made on a different piece of the wire, the surface of which varied from test to test, that was about the limit of experimental accuracy although many results did show better agreement.

The transition pressures rose rapidly with rise in temperature. This large temperature coefficient was doubtless due to two factors: changes in the adsorbed layer, and an increased activity of the ions of the activating electrolyte in the chromic acid solution.

Solutions having a high concentration of chromic acid were found to be most suitable. They were less sensitive to changes in the amount of activating electrolyte and the transition pressures occur in a measurable range at ordinary temperatures. The transition pressures were determined for several temperatures using a solution having the composition: CrO_3, 50.5%; H_2SO_4, 6.5%; H_2O, 43.0%. This was designated as solution No. 1. The data obtained with this solution are reported in Table I and Fig. 2.

TABLE I

PASSIVIFYING PRESSURE OF AIR FOR SOLUTION NO. 1 AT VARIOUS TEMPERATURES

Temp., °C.	19.9	20.5	21.6	22.6	23.0	23.9
Pres., mm.	51	88	112	115	140	153
Temp., °C.	24.5	25.1	29.1	29.6	34.0	34.3
Pres., mm.	200	200	277	300	368	395

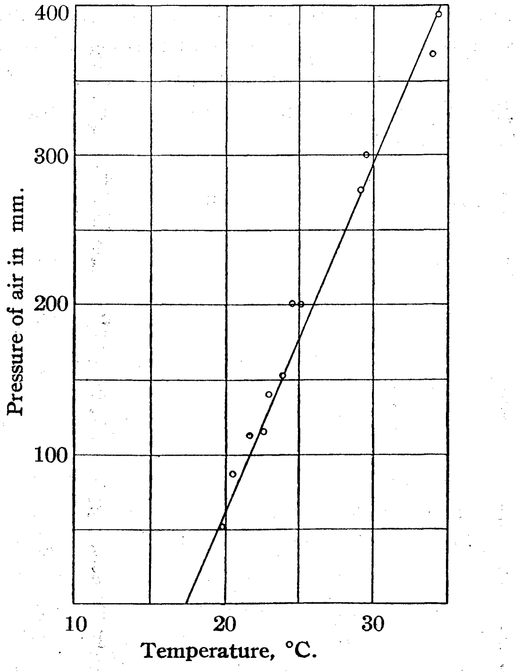

Fig. 2.—Passivifying pressures of air for solution No. 1 at various temperatures.

Similar data were obtained for a solution having the composition: CrO_3, 44.5%, H_2SO_4, 8.3%; HNO_3, 0.2%;

TABLE II

PASSIVIFYING PRESSURE OF AIR FOR SOLUTION NO. 2 AT VARIOUS TEMPERATURES

Temp., °C.	19.1	19.7	19.8	20.4	25.8	30.8	33.0
Pressure, mm.	101	140	140	150	300	565	683

H_2O, 47.0% (solution No. 2) and is shown in Table II and Fig. 3.

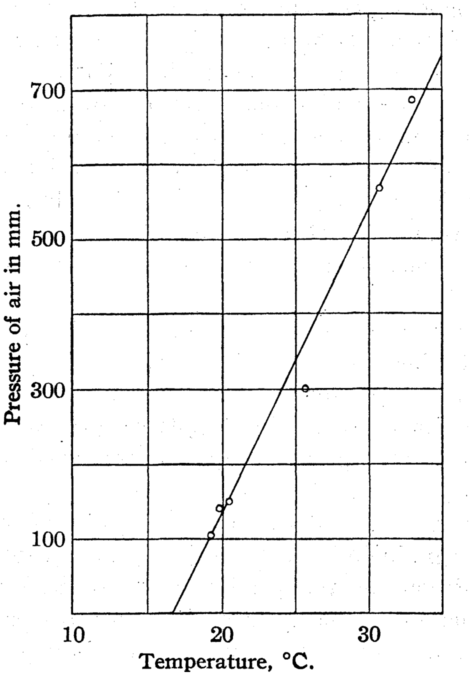

Fig. 3.—Passivifying pressure of air for solution No. 2 at various temperatures.

When oxygen was substituted for air in the apparatus the transitions took place at much lower pressures as shown in Table III and Fig. 4.

TABLE III

PASSIVIFYING PRESSURE OF OXYGEN FOR SOLUTION NO. 1 AT VARIOUS TEMPERATURES

Temp., °C.	23.8	24.5	25.7	25.9	28.5	30.7
Pressure, mm.	40	58	60	63	81	122

When iron was suspended in an atmosphere of hydrogen for a few minutes and then lowered into a chromic acid–electrolyte solution, it was active. To show that this effect was not due to hydrogen dissolved in the chromic acid–electrolyte solution a piece of wire was covered completely with the solution which was then saturated with hydrogen. The iron remained passive. If, however, the iron was raised above the solution into the hydrogen atmosphere and allowed to drain thoroughly it became and remained active when again immersed in the solution. Iron which had been in a hydrogen atmosphere did not become active in solutions of pure chromic acid.

Some experiments were made to determine whether or not a coating of iron oxide would make the iron passive in a suitable chromic acid–electrolyte solution. Iron which was permitted to rust until covered with ferric oxide or heated in air and oxidized to give a bluish color was, after exposure to air, placed in solution No. 1 and also in a 50% solution of pure chromic acid. The oxide readily dissolved in both solutions leaving passive metal with a bright clean surface. When oxidized iron was put under reduced pressure (20 mm.) and then solution No. 1 admitted, the iron oxide dissolved, the metal was active and underwent total dissolution. These results indicate that the cause of passivity of iron in these chromic acid solutions is not an oxide film.

Solutions of chromic acid containing phosphoric acid or sodium sulfate show the same behavior as those containing sulfuric acid. For example, a solution containing 50.7% CrO_3, 8.6% Na_2SO_4, 40.7% H_2O had a transition pressure in air of 70 mm. at 28.7° while a solution containing CrO_3, 50.5%; H_3PO_4, 6.5%; H_2O, 43.0% gave under similar conditions a transition pressure of 150 mm. at 26°.

That this phenomenon of activation by reduced pressure extends over a wide range of concentration of chromic acid is illustrated by a solution having the composition CrO_3, 24.0%; H_2SO_4, 8.0%; H_2O, 68%. The transition pressure in air was 460 mm. at 22°.

To make sure that the results were not influenced by the electromagnetic fields in the apparatus a few points were checked in an apparatus free from all electrical circuits. The method was slow and laborious but sufficient data were obtained to show that the electric and magnetic fields produced no noticeable effect.

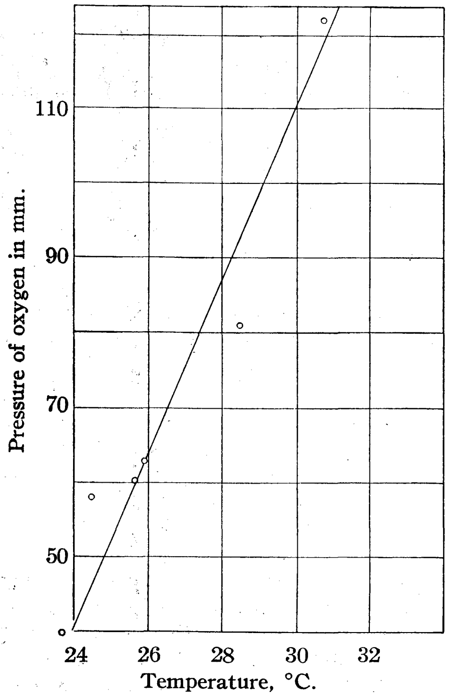

Fig. 4.—Passivifying pressures of oxygen for solution No. 1 at various temperatures.

Adsorption of Oxygen by Iron

Since the experiments described above show that oxygen plays a dominant role in the production of passivity in the chromic acid-electrolyte solutions, it was deemed advisable to determine the extent and reversibility of the adsorption of oxygen on an iron surface of the type under consideration. The apparatus was patterned after that used by Benton and White.[3] Provision was made for the collection and measurement of the gas as it came from a Töpler pump.

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(3) Benton and White, THIS JOURNAL, **52**, 2325 (1930).

The oxygen was prepared by decomposing potassium chlorate. The gas was washed thoroughly and dried before it was admitted to the adsorption chamber.

Nitrogen of excellent commercial grade, which had been passed over copper at 400° to remove traces of oxygen, was used to determine the free space in the apparatus.

The iron sample was prepared by cutting 50 g. of the No. 30 iron wire into very short lengths. This was cleaned thoroughly and then heated *in vacuo* for seventy-two hours under a reduced pressure of 10^{-2} mm. No provision was made for the reduction of any invisible oxide that may have been formed by the brief contact with air because the desire was to have a surface similar to that which had been used in the previously described experiments. It is also somewhat doubtful whether the iron was completely outgassed under these conditions. The complete removal of oxygen was hardly necessitated, however, because the object was the determination of measurable adsorption in the region of transition pressures. The results of a typical run are shown in Table IV.

Table IV

Adsorption of Oxygen by 50 Grams of Iron at 25°

Pressure, mm.	Cc. adsorbed (standard conditions)	Pressure, mm.	Cc. adsorbed (standard conditions)
4.0	0.07	313.5	0.21
11.0	.13	411.7	.23
51.5	.17	515.0	.29
107.3	.18	639.0	.42
195.1	.15	682.0	.49
252.3	.17		

No high degree of accuracy is claimed in the low pressure region, but above 200 mm. very concordant results were obtained. The adsorption was found to be reversible. All of the oxygen entering the apparatus could be recovered at the end of a run within the limits of the reading of the buret. There were no visible signs of oxide formation even after repeated runs on the same sample of iron. Calculations made indicated that the adsorbed layer might be several molecules deep.

A few experiments were made to determine the effect of reduced pressure on iron in nitric acid. If the pressure in a small vessel containing a piece of iron wire was reduced to about 2 mm. and then concentrated nitric acid (sp. gr. 1.42) allowed to flow in around the wire, the iron became active and dissolved completely provided the capacity of the pump was great enough to pump off the gases as fast as they were formed.

These results agree with the work of Freundlich, Patscheke and Zocher[4] in which they found that slow filling of evacuated vessels, containing iron mirrors, with nitric acid caused greater activity than when they were filled rapidly.

The differences which they observed between the "vacuum mirrors" and the "air mirrors" were probably due to the oxygen remaining on the iron which can only be removed by heating to about 300° under pressures of 10^{-2} mm.

Discussion of Results

These experiments show that iron is passive in solutions of chromic acid at all concentrations. No evidence was found of periodic passivity which occurs in certain concentrations of nitric acid. If the chromic acid contains a sufficient concentration of activating ions the concentration of the oxygen surrounding the iron is the factor which determines whether it will be active or passive when placed in solution. That this effect of oxygen is due to adsorption is indicated by the adsorption data. It should be noted, however, that while the adsorption apparatus was as dry as it was possible to make it, water vapor was necessarily present in the other apparatus. To what extent this water vapor affects the adsorption of oxygen is not known.

From this and the previous work the writers have gradually come to the belief that the primary condition for the passivification of iron is the formation on the surface of an adsorbed layer of oxygen or of a "two dimensional compound" of oxygen and iron.[5] Definite oxides may be formed subsequently, particularly in the case of anodic passivation. Such oxides are readily soluble, however, in the acidic solutions used by the authors. Evans[6] has succeeded in isolating these films of oxide from iron which had been treated with various passivifying agents but his experiments fail to prove that these films were the primary cause of passivity. The fact that an oxide-covered iron wire may be made active or passive in chromic acid–electrolyte solutions by merely changing the pressure on the iron before immersion in the liquid makes it appear doubtful whether the oxide layer is an essential factor for passivification in these media.

Summary

1. Iron under reduced pressure becomes active when placed in solutions of chromic acid containing sulfuric acid or other activating electrolytes. In pure chromic acid solutions iron does not become activated by reduction of pressure.

2. The pressure of air or oxygen required to produce passivity increases rapidly with rise in temperature.

3. An atmosphere of hydrogen causes iron to be active in a chromic acid–electrolyte solution.

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[4] Freundlich, Patscheke and Zocher, *Z. physik. Chem.*, **128**, 321 (1927); *ibid.*, **130**, 289 (1927).

[5] See Fredenhagen, *ibid.*, **43**, 1 (1903); **63**, 1 (1908); Evans, *Trans. Faraday Soc.*, **18**, 6 (1922).

[6] Evans, *J. Chem. Soc.*, 1020 (1927); 2651 (1929).

4. Data on the adsorption of oxygen by iron have been given.

5. Oxides of iron were found to be soluble in chromic acid solutions and oxide-covered wires could be made active by a reduction of pressure.

6. An adsorbed film of oxygen as a primary cause of passivity has been discussed.

SEATTLE, WASH. RECEIVED MARCH 31, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CITY COLLEGE OF NEW YORK]

Organic Reagents[1] in Qualitative Analysis. III. The Analysis of the Common Metals of the Alkaline Earth Group and Magnesium Using 8-Hydroxyquinoline

BY LEO LEHRMAN, M. MANES AND J. KRAMER

In the field of qualitative analysis the detection of the alkaline earth metals, especially in small amounts, is one of the most difficult of all. Though a number of organic reagents have been suggested for this purpose, most of them have certain disadvantages which prevent their use in a scheme of analysis. Either they are not specific, or the presence of some other normally occurring metal interferes or else the reagent cannot be employed for separations. However, one organic substance, 8-hydroxyquinoline (oxin, 8-quinolinol), which has already been used as a precipitant for metals,[2] was found to be excellent reagent in the analysis of the group.

In this work a method of analysis of the alkaline earth metals and magnesium, using 8-hydroxyquinoline, has been developed which makes it possible to detect small amounts. In brief Ca^{++} and Mg^{++} are precipitated by the organic reagent in an ammoniacal solution containing ammonium salts. The Ca^{++} is then separated from Mg^{++} in acetic acid as the oxalate and the Mg^{++} reprecipitated as the 8-hydroxyquinoline salt by making the solution alkaline with ammonia. A distinct advantage of the use of 8-hydroxyquinoline is that any excess in the filtrate can be removed easily by evaporation, as it is apparently volatile with steam. The solution is then analyzed for Ba^{++} and Sr^{++} by one of the usual methods.

Together with the scheme of analysis a test has been worked out using tannic acid in an alkaline solution,[3] which gives a preliminary indication of the alkaline earth metals.

Experimental

1. Reaction of Alkaline Earth and Alkali Metals with Tannic Acid in Alkaline Solution.—To varying amounts from 1–500 mg. of the metals, separately, 1 ml. of 2% tannic acid solution was added and then made alkaline with 6 *M* sodium hydroxide solution. Ba^{++}, Sr^{++} and Ca^{++} gave blue-green solutions or precipitates while the others were tan colored; 1 mg. of Ba^{++}, Sr^{++} or Ca^{++} in the presence of 500 mg. of the others, except NH_4^+ gave the same result. When ammonium salts are present the solution is made distinctly alkaline with sodium hydroxide, carefully warmed until all the ammonia is volatilized and then the test is carried out. Thus 1 mg. of Ba^{++}, Sr^{++} and Ca^{++} in the presence of 500 mg. NH_4^+ gave a positive result.

2. Reaction of Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++} with 8-Hydroxyquinoline.—Varying amounts from 1–500 mg. of each of the above, separately, were mixed with 5–30 ml. of saturated ammonium chloride solution, made alkaline with ammonia and 15% solution of 8-hydroxyquinoline in 6 *M* acetic acid[4] added, keeping the solution alkaline with concentrated ammonia, until no further precipitation took place. This is indicated by a yellow supernatant liquid. In order to distinguish a precipitate of a metal 8-hydroxyquinoline compound from that of the reagent itself, at first the solution was kept above the melting point, 73–74°, of the 8-hydroxyquinoline. However, it was found that the calcium salt is appreciably soluble in the hot solution. So, instead, a preliminary test was made using a saturated solution of the reagent in concentrated ammonia. The results of these experiments showed that Ca^{++} and Mg^{++} are completely precipitated while Ba^{++} and Sr^{++} are not precipitated at all.

Using the same procedure and various combinations of the metals, it was found that 1 mg. or more of Ca^{++} and Mg^{++} could be separated completely from 500 mg. of Ba^{++} or Sr^{++} or any combination of both. Similar results were obtained using Na^+ and K^+ instead of Ba^{++} and Sr^{++}.

However, when large amounts of Ca^{++} and Mg^{++} were precipitated in the presence of large amounts of Ba^{++} and Sr^{++}, as much as 5 mg. of Ba^{++} and Sr^{++} was adsorbed by the precipitate. Furthermore, in the presence of 500

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[1] Most of the organic reagents are made by the Eastman Kodak Co., Rochester, N. Y.

[2] "Organic Reagents for Metals," Hopkin & Williams, Ltd., London, Eng., p. 51.

[3] L. Rosenthaler, *Mikrochemie*, **14**, 363–368 (1934); G. Ammer and H. Schmitz, *Wasser*, **8**, II, 161–168 (1934).

[4] This solution was chosen in preference to alcohol and diluted acetic acid solutions as a result of experiments showing less volume of the precipitant would be necessary.

mg. of Ca^{++} or Mg^{++} or combination of both, only 2 mg. of Ba^{++} or 3 mg. of Sr^{++} in the original solution could be detected after the precipitation.[5]

3. **Separation of Ca^{++} and Mg^{++}.**—Various combinations of Ca^{++} and Mg^{++} from 1–500 mg. in a saturated ammonium chloride solution were precipitated with 8-hydroxyquinoline, keeping the solution alkaline with ammonia, filtered with suction and then dissolved with hot 3 *M* acetic acid. While still hot 0.25 *M* ammonium oxalate solution was added slowly with stirring until no further precipitation of the Ca^{++} took place. The mixture was filtered, the filtrate concentrated to 10 ml. by evaporation and divided in half. One half was tested for Mg^{++} with *p*-nitrobenzene–azoresorcinol and sodium hydroxide[6] and the other half by making alkaline with ammonia and adding a small volume of 8-hydroxyquinoline solution. The experiments showed that 1 mg. of either metal could be detected in the presence of 500 mg. of the other.

4. **Separation of Ba^{++} and Sr^{++}.**—Though this method is a standard one, experiments were carried out to determine how much of each could be detected. Different mixtures containing 1–500 mg. of each were precipitated with 2 *M* ammonium carbonate, filtered and dissolved in 1 *M* acetic acid. The solution was warmed and 0.5 *M* potassium chromate solution added slowly with stirring until no further precipitation occurred. After filtering, washing and concentrating the filtrate, it was tested for Sr^{++} with ammonium oxalate solution. The results showed that 1 mg. of either metal could be detected in the presence of 500 mg. of the other.

On the basis of the above experiments a method of analysis was worked out and various combinations of the four metals from 1–500 mg. analyzed. The results confirmed those found above, *viz.*, that 1 mg. of Ca^{++} and Mg^{++} could be detected in the presence of 500 mg. of any other or combination of others; that 2 mg. of Ba^{++} and 3 mg. of Sr^{++} are detectable in the presence of 500 mg. of Ca^{++} or Mg^{++} or combination of both.

5. **Method of Analysis.**—The filtrate from the ammonium sulfide group, after acidification with acetic acid and removal of hydrogen sulfide, is evaporated to 25 ml. and filtered, if necessary. A small portion, 5 ml., is made alkaline with concentrated ammonia and a saturated solution of 8-hydroxyquinoline in ammonia added to test for the presence of Ca^{++} and Mg^{++}. If present, the test portion is combined with the main solution, made alkaline with concentrated ammonia and 15% solution of 8-hydroxyquinoline in 6 *M* acetic acid slowly added, keeping the solution alkaline with concentrated ammonia, until no further precipitation occurs. This is indicated by a yellow supernatant liquid. The mixture is filtered using suction and the precipitate washed twice with dilute ammonia, the washings being combined with the filtrate (filtrate B).

Residue.—The precipitate is dissolved in the smallest volume of hot 3 *M* acetic acid. While still hot, 1 *M* ammonium sulfate solution is added slowly with stirring to precipitate any Ba^{++} and Sr^{++} that had been adsorbed,[7] the solution filtered, the residue washed and then discarded. The filtrate is heated and 0.5 *M* ammonium oxalate solution slowly added with stirring until no further precipitation, showing the presence of Ca^{++}, takes place, filtered and washed (filtrate A).

Filtrate A.—A small portion is first tested for magnesium with *p*-nitrobenzene-azoresorcinol and sodium hydroxide. If positive, the remainder of the solution is made alkaline with ammonia and a small volume of the 8-hydroxyquinoline solution added, keeping the solution alkaline with ammonia. A yellow precipitate indicates Mg^{++}.

Filtrate B.—The solution is evaporated to dryness and the ammonium salts volatilized by continual heating. After cooling, the residue is treated with a small amount of dilute hydrochloric acid and then a small volume of water is added. The solution is filtered, if necessary, and the filter paper washed. The solution is made alkaline with concentrated ammonia and ammonium carbonate added until no further precipitation occurs, filtered and washed (filtrate contains alkali group).

Residue.—Dissolve with 1 *M* acetic acid and test a small portion for Ba^{++} with 0.5 *M* potassium chromate solution.[8] If present, warm the solution and add the potassium chromate solution slowly until no further precipitation takes place. Filter and wash. The filtrate is evaporated to 10 ml. and 0.5 *M* ammonium oxalate solution added, a white precipitate indicating Sr^{++}.

Summary

A preliminary test, using tannic acid, has been worked out, which can indicate 1 mg. of the alkaline earth metals even in the presence of large amounts of ammonium salts.

A method of analysis of the alkaline earth metals and magnesium, using 8-hydroxyquinoline, has been developed so that 1 mg. of Ca^{++} and Mg^{++}, 2 mg. of Ba^{++} and 3 mg. of Sr^{++} can be detected in the presence of 500 mg. of any other metal of this group or combination of others.

In the method of analysis Ca^{++} and Mg^{++} are separated from Ba^{++} and Sr^{++} by precipitating with 8-hydroxyquinoline in an ammoniacal solution. The Ca^{++} is separated from Mg^{++} as oxalate in acetic acid and the magnesium reprecipitated as the 8-hydroxyquinoline salt by making alkaline with ammonia. Ba^{++} and Sr^{++} are analyzed by one of the usual accepted methods.

NEW YORK, N. Y. RECEIVED FEBRUARY 13, 1937

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[5] If the Ca^{++} and Mg^{++} 8-hydroxyquinoline precipitates are dissolved in acetic acid and reprecipitated with ammonia all the adsorbed Ba^{++} and Sr^{++} can be removed.

[6] (a) K. Suitzu and K. Okuma, *J. Soc. Chem. Ind., Japan*, **29**, 132 (1926); (b) Feigl, "Qualitative Analyse mit Hilfe von Tüpfel-Reaktionen," Akademische Verlagsgesellschaft, Leipzig, Germany, 1935, 2d ed., p. 262.

[7] As the largest amount of Ba^{++} and Sr^{++} adsorbed does not exceed 5 mg., only a small volume of ammonium sulfate solution is necessary and practically no Ca^{++} is precipitated. If very small amounts of Ba^{++} and Sr^{++} are to be detected, the 8-hydroxyquinoline precipitate should be dissolved in acetic acid and reprecipitated with ammonia.

[8] If Ba^{++} is absent, a sensitive test for Sr^{++} can be immediately performed by treating with a saturated water solution of tetrahydroxyquinone, a reddish-brown precipitate indicating its presence [G. Gutzeit, *Helv. Chim. Acta*, **12**, 728 (1929)].

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. VII. Alkyl- and Arylpropiolnitriles. Resonance in the Acetylene Triple Bond

BY B. C. CURRAN AND H. H. WENZKE

The low moments of the halogenoacetylenes in comparison to those of the alkyl halides point to a probable resonance of the classical structures with the form $R—C^{-}=C=X^{+}$. Resonance of the —C≡C— group could be established more definitely by the examination of a class of compounds wherein the effect would be to increase the moment. The acetylenic nitriles offer a good test for this resonance in that the two forms contributing to the molecule would be R—C≡C—CN and $R—C^{+}=C=C=N^{-}$. That the comparison of the moments of acetylenic halides and nitriles is further opposite is evident from an analysis of the data of Table I. In these compounds the polarity of which is influenced only by induction, the increase in moments from the acids to the substituted butanes is seen to be roughly parallel. The inductomeric polarizabilities of the —CN and —Cl groups are thus very nearly the same.

TABLE I

ELECTRIC MOMENTS OF ALKYL CHLORIDES AND CYANIDES[1] × 10^{18}

	Chlorides	Δμ	Cyanides	Δμ
Hydrogen	1.03	0.83	2.65	0.79
Methyl	1.86	0.18	3.44	0.13
Ethyl	2.04		3.57	
Propyl	2.04		3.57	
Butyl	2.04		3.57	

Preparation of Compounds.—The butyl-, amyl- and phenylpropiolnitriles were prepared by the reactions of the corresponding acetylene magnesium bromides with cyanogen chloride.[2] The *p*-tolyl propiolnitrile was prepared by the following method. *p*-Tolylaldehyde was converted into *p*-methyl ethyl cinnamate by the action of ethyl acetate in the presence of sodium.[3] The cinnamate was brominated in the cold, dehydrohalogenated with alcoholic potassium hydroxide, acidified with hydrochloric acid, and the resulting *p*-tolylpropiolic acid esterified with methyl alcohol. The ester was dissolved in excess alcoholic ammonium hydroxide and allowed to stand in a stoppered flask for one month. The alcohol was then removed by distillation, and the amide was first dried and then converted into the nitrile by the action of phosphorus pentoxide.[4] The phenyl- and *p*-tolylpropiolnitriles were purified by repeated crystallizations from petroleum ether in a bath of liquid ammonia, and dried for a few hours by a current of dry air before being placed in a desiccator over calcium chloride. The polarizations at infinite dilution were obtained by the method of Hedestrand.[5] The value of the electronic polarization of phenylpropiolnitrile was obtained from the literature, and from this the value for *p*-tolylpropiolnitrile was calculated.

TABLE II

PHYSICAL CONSTANTS OF R—C≡C—CN

R	°C.	n_{D25}	d^{25}_4
C_4H_9	B. p. 69.7–70.5 (25 mm.)	1.44673	0.84124
C_5H_{11}	B. p. 74–75 (12 mm.)	1.45021	.84325
C_6H_5	M. p. 38	....	....
p-$CH_3C_6H_4$	M. p. 52	....	....

TABLE III

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF ACETYLENIC NITRILES

Solvent, benzene; temp. 25°

c_2	ε	d
	Butylpropiolnitrile	
0.00000	2.2760	0.87340
.01763	2.7103	.87251
.02156	2.8070	.87200
.02224	2.8271	.87196
	Amylpropiolnitrile	
0.00000	2.2760	0.87340
.01994	2.7715	.87236
.02238	2.8301	.87231
.02384	2.8673	.87210
	Phenylpropiolnitrile	
0.00000	2.2760	0.87364
.01435	2.6928	.87671
.01463	2.7018	.87717
.01807	2.7968	.87730
	p-Tolylpropiolnitrile	
0.00000	2.2760	0.87364
.01697	2.8596	.87601
.02188	3.0205	.87747
.02259	3.0432	.87770

TABLE IV

POLARIZATIONS AND MOMENTS OF ACETYLENIC NITRILES

—Propiolnitrile	P_∞	MR_D	P_{A+M}	$10^{18}\ \mu$
Butyl	400.6	33.99	366.6	4.21
Amyl	406.8	38.61	368.2	4.22
Phenyl	462.1	42.39	419.7	4.50
p-Tolyl	543.4	47.01	496.4	4.90

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(1) Cowley and Partington, *J. Chem. Soc.*, 604 (1935).

(2) Grignard and Courtot, *Bull. soc. chim.*, **17**, 228 (1915).

(3) Marvel and King, "Organic Syntheses," **9**, 38 (1929).

(4) Moureu and Lazennec, *Bull. soc. chim.*, **35**, 524 (1906).

(5) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

TABLE V

ELECTRIC MOMENTS OF CHLORIDES AND NITRILES

Compound	10^{18} μ	Compound	10^{18} μ
Chlorobutane	2.04	Valeronitrile	3.57
Chlorobenzene[6]	1.56	Benzonitrile[6]	3.91
Butylchloroacetylene[7]	1.23	Butylpropiolnitrile	4.21
Phenylchloroacetylene[8]	1.10	Phenylpropiolnitrile	4.50

Discussion

The large moments found for the acetylenic nitriles reveal the existence of resonance in these compounds as well as in the halogenoacetylenes. From Table V it can be seen that butylchloroacetylene has a lower moment than chlorobenzene, while butylpropiolnitrile has a higher moment than benzonitrile. These comparisons indicate that the forms $R-C^{-}=C=Cl^{+}$ and $R-C^{+}=C=C=N^{-}$ contribute to a greater extent to their respective molecules than do the forms $^{-}C_6H_5=Cl^{+}$ and $^{+}C_6H_5=C=N^{-}$. The electromeric polarizability of the acetylene triple bond is therefore greater than that of the phenyl group. A pronounced increase in moment is obtained by replacing a phenyl group for an alkyl group in the acetylenic nitriles despite the fact that the alkylacetylenes have higher moments than phenylacetylene. While this increase is due partly to the fact that the form $^{+}C_6H_5=C=C=C=N^{-}$ is more polar than $R-C^{+}=C=C=N^{-}$ it is also evidence of the strong resonance in phenylpropiolnitrile.

Summary

1. Electric moments have been determined for butyl-, amyl-, phenyl- and *p*-tolylpropiolnitriles.

2. The values obtained for these moments prove the existence of resonance in these molecules as well as in the alkyl and aryl halogenoacetylenes.

3. The electromeric polarizability of the acetylene triple bond is shown to be greater than that of the phenyl group.

NOTRE DAME, INDIANA RECEIVED MARCH 22, 1937

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[6] Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, 1931, 203.

[7] Pflaum and Wenzke, THIS JOURNAL, **56**, 1106 (1934).

[8] Wilson and Wenzke, *ibid.*, **56**, 2024 (1934).

NOTES

Photosynthesis and the Absorption of Radiation by Plants

BY G. RICHARD BURNS

In the course of investigations on the amount of photosynthesis by white pine seedlings in different portions of the spectrum, a rather interesting correlation was found between the amount of photosynthesis and the color of the plant.

In an attempt to arrive at some value for the radiation absorbed by the plant the reflection of the plant was assumed to be the reflection of the needles to light of 45° incidence and the absorption, the absorption of the plant pigments in acetone solution with the concentration the same as in the plant. The absorption spectrum obtained from these two values might be called the "primary absorption spectrum" of the plant, defining the difference between this and the true absorption as the "secondary absorption." The values for the secondary absorption would be high where the primary is low due to reflection within the needle. Also the absorption of the pigments is shifted toward the blue when in solution. In determining the absorption and reflection values, each spectrometer reading covered a wide band of wave lengths and the front slit was 0.75 mm. wide so that the spectrum was rather blurred.

Graph I gives the percentage primary absorption for two types of seedlings, B for those grown in blue light and R for those grown in red. The stepwise curves indicate, approximately, the range of wave lengths covered at each reading. Assuming constant quantum efficiency and that only light thus primarily absorbed is effective in photosynthesis it is possible to calculate the relative amounts of photosynthesis in any two portions of the spectrum. These values calculated from the rough physical measurements agree within a few per cent. with the experimentally determined values in all cases. Thus these primary absorption curves may be considered as representing the relative amounts of photosynthesis at equal incident quantum intensity.

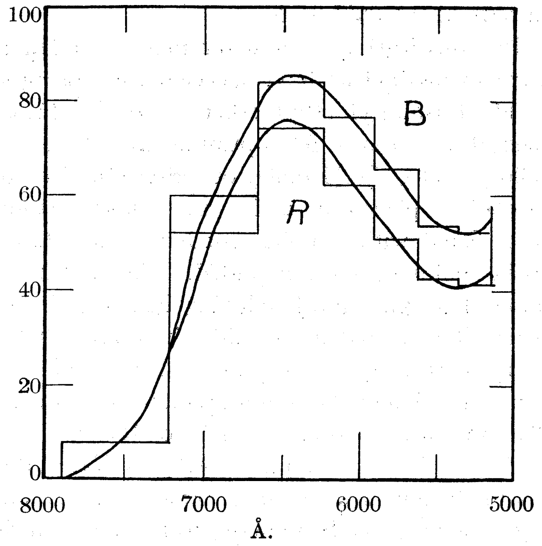

Fig. 1.

The fact that the amount of photosynthesis depends on the primary absorption spectrum seems fairly well established since the relationship holds for a large number of experiments with different ranges of wave lengths and different colors of trees as well as with experiments with semi-monochromatic radiation from filtered sodium and mercury sources. It offers a quantitative explanation of all our experimental results, published in botanical journals from 1933 on.

Just why the amount of photosynthesis should agree with this arbitrary value rather than with the true absorption is still a matter of speculation.

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Received January 25, 1937

Diazo Coupling of 5-Hydroxy-6-methylhydrindene

By Louis F. Fieser and Warren C. Lothrop

In a previous report [This Journal, **58,** 2050 (1936)] we stated that the above compound (I) failed to couple with diazotized *p*-nitroaniline in alkaline solution, whereas in parallel tests 5-hydroxy-4,7-dimethylhydrindene and 6-hydroxy-5,8-dimethyltetralin coupled readily under the same conditions. On preparing a further quantity of I in order to investigate its behavior with other coupling agents, we first tried to effect a coupling with diazotized *p*-nitroaniline under other conditions and found that this indeed can be accomplished. Each of seven solutions containing 0.1 g. of I in 10.5- to 20-cc. portions of sodium hydroxide solutions of concentrations varying from 0.119 to 2.49 *N* was treated at 0° with 2.5 cc. of an aqueous solution containing approximately one equivalent of the diazo compound and 0.000021 mole of hydrochloric acid, and after ten minutes the mixtures were boiled and the precipitate collected. The crude *p*-nitrobenzeneazo derivative of I (m. p. 210–215°) was obtained in yields decreasing steadily from 36% in the most weakly alkaline medium to a negligible amount (*ca.* 1%) in the most alkaline solution. The purified azo compound formed brown-red needles, m. p. 230–232° (calcd.: C, 64.63; H, 5.08. Found: C, 64.32; H, 5.34). Similar results were obtained even with aniline, the benzeneazo compound forming red needles, m. p. 141–143° (calcd.: C, 76.16; H, 6.39. Found: C, 75.97; H, 6.60).

We are investigating the conditions of the couplings more fully and making a further comparison with related compounds; but it seems desirable to correct at once the impression given in the earlier report that the hydrindene derivative I departs entirely from the behavior characteristic of a phenol having a free ortho position.

Converse Memorial Laboratory
Harvard University
Cambridge, Massachusetts

Received March 29, 1937

Allomucic Acid

By Fred L. Humoller and Wm. F. McManus

Recently we published a paper on the preparation of new derivatives of *l*-allonic and *l*-altronic acids. While we were mainly concerned in this paper with the interesting behavior of allonic acid and its lactones, we also described briefly several new compounds related to the above two acids, among them allomucic acid. Dr. Th. Posternak has been kind enough to point out to us that in 1935 he had published an account of the preparation of allomucic acid from *d*-allonolactone. Unfortunately we had overlooked this publication[1] and the statement in our publication, "Posternak did not report, however, the preparation of allomucic acid," does a grave injustice to Dr. Posternak. After having read his paper no one can doubt Dr. Posternak's claim of priority of the preparation of allomucic acid.

[1] Posternak, *Helv. Chim. Acta*, **18**, 1283 (1935).

LOYOLA UNIVERSITY
SCHOOL OF MEDICINE
CHICAGO, ILL.
RECEIVED FEBRUARY 27, 1937

Hydrogen-Deuterium Exchange in Acetate Solution

BY SYLVESTER LIOTTA AND VICTOR K. LA MER

In the course of a study of acetate-ion catalyzed reactions in heavy water, it became necessary to determine the extent of the exchange between the hydrogens of the methyl group and the deuterium of the solvent. From the results of early investigations[1,2,3] little or no exchange was to be expected, while from later work[4,5] varying degrees of exchange could be expected, depending upon temperature and time of contact.

Heavy water (d^{25}_{25} 1.1000, approximately 93% D) was purified by distillation *in vacuo* to remove possible catalysts. Anhydrous sodium acetate was added to produce a 10% solution. After standing for two weeks in a Pyrex vessel at 25–30°, the solvent was recovered by distillation *in vacuo*. The density was redetermined by filling the same pycnometer. Sodium acetate and acetic anhydride were then added to make a final concentration of 10% and 1%, respectively. After two weeks at 25–30°, the solution was neutralized with caustic soda and the same procedure repeated.

Solvent before addn. of sodium acetate, g.	10.5417
Solvent after first distn., g.	10.5413
Solvent after second distn., g.	10.5420

If any exchange occurs either in slightly acid or slightly alkaline solution at room temperature it is exceedingly slow.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.
RECEIVED FEBRUARY 24, 1937

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[1] Bonhoeffer, *et al.*, *Z. physik. Chem.*, **B23**, 171 (1933).

[2] Lewis and Schutz, THIS JOURNAL, **56**, 493 (1934).

[3] Klar, *Z. physik. Chem.*, **B26**, 335 (1934).

[4] Hall, Bowden and Jones, THIS JOURNAL, **56**, 750 (1934).

[5] Wynne-Jones, *Chem. Rev.*, **17**, 115 (1935). Results of Turkevich. Table 3, 200 hrs. at 80° yields 85% exchange.

An Improved Method for Synthesizing Isobutyl Ethyl Ether

BY E. M. MARKS, DAVID LIPKIN AND BERNARD BETTMAN

According to Cerchez[1] aliphatic ethers can be synthesized from alkyl sulfates and magnesium alcoholates. In several instances he obtained yields of 60–70%. In preparing isobutyl ethyl ether by this method from diethyl sulfate and magnesium isobutylate, we obtained the product in only about 30% yield.

By substituting sodium for magnesium in the Cerchez method we have succeeded in raising the yield of isobutyl ethyl ether to 70%. Experimental conditions for optimum results are as follows: 93 g. (1.25 mole) of anhydrous isobutyl alcohol is placed in a 500-ml. round-bottomed flask fitted with a reflux condenser and 12.5 g. (0.54 mole) of sodium added. The mixture is allowed to react until refluxing has ceased, after which it is heated in an oil-bath at 120–130° for two and three-quarters hours. At the end of this time a portion of the sodium remains undissolved. The mixture is then cooled to 105–115° and 77.1 g. (0.5 mole) of pure diethyl sulfate added gradually during a two-hour period. Reaction is vigorous and steady refluxing takes place during addition of the sulfate. After all has been added, refluxing is continued for two hours. The reaction mixture is then permitted to cool to room temperature (overnight) after which an equal weight of crushed ice is added, followed by a slight excess of dilute sulfuric acid. The ether is then steam-distilled out of the flask, separated from the aqueous portion of the distillate, given three equal-volume washes of 30% sulfuric acid, to remove most of the unreacted isobutyl alcohol, washed twice with water and dried over anhydrous potassium carbonate. The dried product is then refluxed over sodium ribbon for three hours to remove all traces of alcohol and finally is distilled through a precision fractionating column of the type recommended by Podbielniak.[2] The yield of isobutyl ethyl ether was 70%, based on diethyl sulfate. The boiling point, density and refractive index of our ether agreed with the recorded values[3] within the experimental error.

Several variables in this synthesis have been studied. (1) If the isobutyl alcohol is not dried rigorously, the yield of ether is reduced to

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[1] Cerchez, *Bull. soc. chim.*, **43**, 762 (1928).

[2] Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 135 (1933).

[3] Norris and Rigby, THIS JOURNAL, **54**, 2088 (1932).

67%. (2) Increasing the quantity of alcohol to 1.5 mole, in an attempt to dissolve more of the sodium, has no appreciable effect on the yield. (3) Prolonged heating of alcohol with sodium (eight hours) results in a darker colored crude product and also a reduction in yield to 65%. It is unnecessary that all of the sodium be dissolved before the diethyl sulfate is added. Apparently as the sodium isobutylate is used up in the reaction, more sodium goes into solution until all is dissolved. (4) A temperature range of 105–140° is permissible during reaction with the diethyl sulfate. If the temperature is kept lower (95°), the yield of ether is reduced (58%). (5) If only the theoretical amount of sodium (0.5 mole) is used, the yield of ether amounts to 65%. (6) Isobutyl alcohol, diethyl sulfate and solid potassium hydroxide react to form isobutyl ethyl ether in 22.5% yield. If the solid alkali is replaced by a 50% aqueous solution, no ether is formed.

It is possible also to synthesize *s*-butyl ethyl ether by this method, using sodium *s*-butylate and diethyl sulfate. Our data at this time are rather incomplete, but indications point to a maximum yield about 48%.

THE ATLANTIC REFINING CO.
PHILADELPHIA, PA.
RECEIVED FEBRUARY 11, 1937

The Solubility of Lithium and Sodium Fluorides

BY JOHN H. PAYNE

In view of the discordancy in the data for the solubility of lithium and sodium fluorides in water,[1] we have conducted careful determinations of these data at 0, 25 and 35°.

Lithium sulfate made from Kahlbaum pure lithium carbonate was recrystallized until the reaction was neutral, and the fluoride precipitated by means of Merck "Zur Analyse" ammonium fluoride. Sodium fluoride was prepared from Kahlbaum pure sodium carbonate and hydrofluoric acid by the method of McAdams and Smith.[2] Both preparations were conducted entirely in platinum. Analysis by conversion to the sulfate gave an average of 99.94% purity. The purity of the fluorides was also checked by a spectroscopic examination. The solubility vessels, coated internally with several layers of a specially purified high-melting paraffin wax, were immersed completely in a thermostat with delivery tubes, also paraffined, to permit the removal of samples without removing the vessels from the thermostat. The samples were rotated for from forty-four to seventy-two hours until equilibrium was reached, then filtered into a 50-cc. pycnometer, also immersed in the thermostat. After weighing, the entire contents of the pycnometer were washed into a platinum vessel, evaporated to dryness, and weighed. All determinations were made in triplicate and equilibrium was approached from both directions in each case. The average deviation of the triplicates was 0.13% and the maximum deviation 0.38%. The thermostat was regulated to within 0.02°.

TABLE I

SOLUBILITY OF LITHIUM AND SODIUM FLUORIDES

	Lithium fluoride		Sodium fluoride	
Temp., °C.	Soly. mole/ 1000 g. water	d_4^t satd. soln.	Soly. mole/ 1000 g. water	d_4^t satd. soln.
0	0.0464	....	0.871	....
25	.0513	0.9984	.983	1.0384
35	.0522	.9958	.989	1.0354

THE UNIVERSITY OF HAWAII
HONOLULU, HAWAII
RECEIVED FEBRUARY 9, 1937

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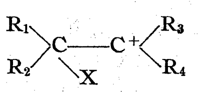
(1) Carter, *Ind. Eng. Chem.*, **20**, 1195 (1928).

(2) McAdams and Smith, THIS JOURNAL, **34**, 593 (1912).

The Halogenation of Ethylenes

BY IRVING ROBERTS AND GEORGE E. KIMBALL

Recent work by Bartlett and Tarbell[1,2] has shown that the first step in the reaction of halogen molecules with the ethylene linkage leads to the formation of a negative halide ion and a positively charged organic ion. This ion has been postulated by Robinson[3] to have the structure



(1)

Some doubt has been cast on this mechanism[4] because of the presumption that there should be free rotation about the C–C single bond, which would lead to a mixture of equal amounts of the *cis* and *trans* halogenation products. In those cases in which the halogenation is homogeneous and not photochemical it is observed that either the *cis* or *trans* halogenation reaction predominates, forming at least 80% of the product.[5] It

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(1) Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

(2) Tarbell and Bartlett, *ibid.*, **59**, 407 (1937).

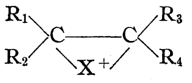
(3) Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London, 1932; Ingold, *Chem. Rev.*, **15**, 225 (1934).

(4) See, *e. g.*, Ogg, THIS JOURNAL, **57**, 2727 (1935).

(5) *Cf.* Freudenberg, "Stereochemie," Verlag Franz Deuticke Vienna, 1933, p. 520. Some of the reactions listed here are photochemical or complicated by side reactions.

has, therefore, been postulated that the second step of the reaction (the addition of halide ion to the positive organic ion) takes place so rapidly that there is not sufficient time for rotation about the single bond to take place.

We would like to point out that free rotation about the C–C bond is *not* to be expected. If this structure is assumed, one of the orbitals of the C^+ must be completely empty. The X atom on the other hand has three orbitals occupied by pairs of electrons. This arrangement is such that a coördinate link will almost certainly be formed by the sharing of one of the pairs of electrons of the halogen with the unoccupied orbital of the carbon. Another possible structure of the ion is one in which the positive charge is on the halogen. The X^+, being isoelectronic with a member of the oxygen family, should show a valence of two, *i. e.*, it should form a structure of the ethylene oxide type



(2)

From an electronic viewpoint structures (1) and (2) are identical. The difference between the ionization potential of carbon (11.22 volts) and that of a halogen (*e. g.*, 11.80 volts for bromine) is so small that the actual structure of the ion is undoubtedly intermediate between (1) and (2). Since the two carbons in either structure are joined by a single bond and by a halogen bridge, free rotation is not to be expected.

If, however, R_1 and R_3 (or R_2 and R_4) are similarly charged groups (*e. g.*, COO^-) there may be sufficient repulsion between them to overcome the restraining force of the double linkage, and rotation to the opposite configuration may take place before the second step of the reaction occurs.

This second step, which may be the addition of either a halogen ion X^- or some other atom or molecule, is probably a simple "three-atom" reaction of the type proposed by London,[6] and developed by Polanyi[7] and Olson.[8] In this case the new atom will approach one of the carbon atoms from the side opposite to the X atom already present. A bond to this carbon will be formed while the bond from the original X to the carbon is broken, with simultaneous neutralization of the charge of the ion. This process will always lead to *trans* addition, except in the previously mentioned case in which there are two like charged groups initially in the *cis* position.

With this modification the mechanism suggested by Robinson and by Bartlett and Tarbell explains all the existing data on the reactions of the halogens with ethylene linkages. The additions of bromine and chlorine to maleic and fumaric acids are very largely *trans*,[9] as the theory predicts. The additions of bromine and chlorine to fumarate ion are again predominantly *trans*, but the addition of bromine or chlorine to maleate ion, with its two negatively charged *cis*-carboxylate ions, is almost entirely *cis*.[10]

The difficulty of explaining the maintenance of configuration in the bromination of stilbene and isostilbene, which yield different methoxybromides and different dibromides[1] no longer exists if this structure of the intermediate ion is postulated. This is also true of the formation of the halo-beta-lactones from dimethylmaleic and dimethylfumaric acids.[2]

The authors wish to thank Prof. L. P. Hammett for his helpful discussions of this problem.

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(6) London, *Z. Elektrochem.*, **35**, 552 (1929).

(7) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); Bergmann, Polanyi, and Szabo, *ibid.*, **B20**, 161 (1933).

(8) Olson, *J. Chem. Phys.*, **1**, 418 (1933); Olson and Voge, THIS JOURNAL, **56**, 1690 (1934).

(9) McKenzie, *J. Chem. Soc.*, **101**, 1196 (1912).

(10) Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925); Kuhn and Wagner-Jauregg, *Ber.*, **61**, 519 (1928).

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

RECEIVED MARCH 4, 1937

A Fermentation Test for Vitamin B_1

BY ALFRED SCHULTZ, LAWRENCE ATKIN AND CHARLES N. FREY

Vitamin B_1 (Merck's natural-crystalline) exerts a powerful action on the rate of alcoholic fermentation. In the presence of a suitable sugar–salt buffer mixture as little as one gamma (0.000001 g.) of the vitamin may be detected.

Table I gives the results of a typical test.

TABLE I

Total volume in each case, 100 cc. (distilled water). Yeast for each, 1 g. commercial bakers' yeast (Fleischmann). Sugar, 3 grams Merck C. P. Dextrose, plus synthetic salt mixture and buffer. Temperature, 30°. Oscillations, 100 per minute.

Natural crystalline vit. B_1 mg.	Cc. of gas in 3 hours
None	185
0.001	215
.005	305
.010	350
.040	395
.100	405

It is natural to suppose that this phenomenon could be employed for vitamin B_1 assay. This has been done and when compared with assay by rat growth test the results so far have shown a very satisfactory concordance. We have been enabled to test synthetic vitamin B_1 (Merck "Betabion") through the courtesy of Merck & Co. The Betabion gives results scarcely distinguishable from the natural crystalline product.

The Fleischmann Laboratories
810 Grand Concourse
New York, N. Y.
Received December 22, 1936

Debromination of Mono and Dibromocholestanone

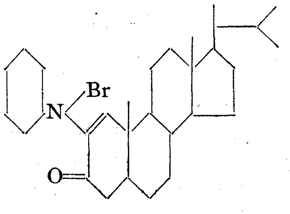
By E. Schwenk and B. Whitman

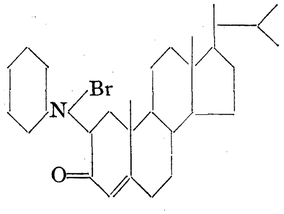
We have been studying for some time the debromination of various sterol bromides, particularly those compounds in which the reaction would lead to unsaturation in the first ring. The appearance of several articles[1] dealing with this subject makes it seem desirable to publish some of our results now.

We have found that the nature of the reagent used to remove hydrogen bromide from bromo sterols has considerable influence on the course of reaction. It is thus possible to obtain several different reaction products from the same bromo compound.

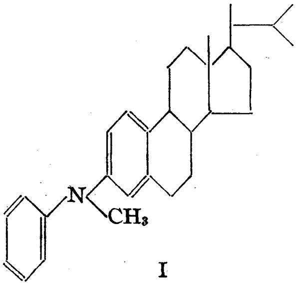
Experiments with mono- and dibromocholestanone are illustrative of this point. From monobromocholestanone, by refluxing with pyridine, we obtained the same pyridinium compound that Butenandt and Wolff[2] reported. However, with dimethylaniline, monobromocholestanone yields mainly cholestanone. In this case the bromine has been replaced by hydrogen. This is the only example of such a reaction of which we are aware.

With dibromocholestanone pyridine yields an unsaturated pyridinium salt, arising very probably by splitting one bromine atom as hydrobromic acid and forming a salt with the other. For the dibromocholestanone, the 2,2,[1b] as well as the 2,4,[1c] position for the bromine atoms has been discussed. Accordingly, the new pyridinium compound derived from dibromocholestanone would have one of the structures

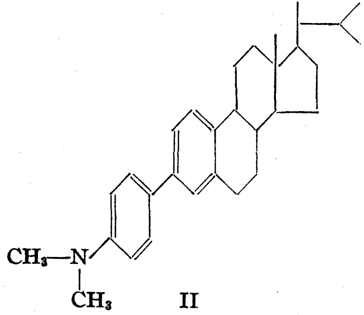




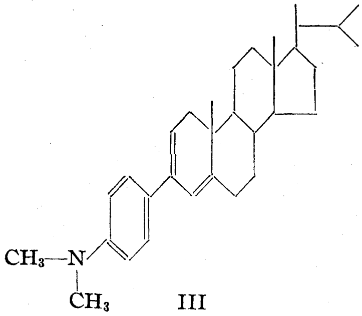
On refluxing dibromocholestanone with dimethylaniline, a substance was obtained which by analysis was found to contain only carbon, nitrogen and hydrogen, but no oxygen. The presence of nitrogen and absence of oxygen suggests that some condensation involving the keto group and the benzene ring has taken place. That such is the case is supported by the fact that this substance gives a beautiful wine-red coupling reaction with nitrodiazobenzene. This acid coupling is typical of an amine. The analytical results point to the substance being either $C_{33}H_{47}N$(I) or $C_{34}H_{49}N$(II) rather than $C_{35}H_{53}N$(III). In our opinion, formula II is the most probable. This would mean that ring A of the cholesterol has become aromatic.



I



II



III

The new substance is distinguished by the fact that its solution in acetic acid couples immediately

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[1] (a) Butenandt and Wolff, *Ber.*, **68**, 2091 (1936); (b) Ruzicka, Bosshard, Fischer and Wirz, *Helv. Chim. Acta*, **19**, 1147 (1936); (c) Butenandt, Schramm, Wolff and Kudszus, *Ber.*, **69**, 2779 (1936).

[2] Butenandt and Wolff, *ibid.*, **68**, 2092 (1936).

on addition of *p*-nitrodiazobenzene solution, giving a beautiful wine-red coloration.[3]

Experimental

I. Five grams of monobromocholestanone is dissolved in 50 cc. of dimethylaniline and heated for eight hours so that the solution boils gently. The reaction mixture is poured into iced hydrochloric acid and the half solid precipitate taken up with ether. The ether solution is washed thoroughly with hydrochloric acid, water, soda solution and again water, dried and evaporated. A brown oil which partly crystallizes is obtained. By dissolving in acetone and chilling crystals are obtained which, by several recrystallizations, become white. They melt at 125–126°. With phenylhydrazine the tetrahydrocarbazol derivative described by Doré and Petrow[4] is obtained, melting point 167–182°. The mixed melting point with the tetrahydrocarbazol derivative m. p. 165.5–181° (Doré and Petrow 180–181°) prepared from pure cholestanone was found to be 168–182.5°. From the tetrahydrocarbazol derivative the picrate was prepared which melted at 208–209.5° (Doré and Petrow 209–210°).

II. Five grams of dibromocholestanone is heated with 50 cc. of pyridine. After a short time (twenty to thirty minutes) the precipitation of white crystals begins and soon the flask is filled with them, so that the mixture starts to bump. It is now cooled, filtered and the crystals washed with alcohol. After one recrystallization from alcohol, in which they are difficultly soluble, white shining needles are obtained which show decomposition above 280°, but no melting point. By pouring alkali on the crystals, they take up a beautiful orange coloration, characteristic of pyridinium compounds. Analysis showed them to contain bromine and nitrogen: calcd. for $C_{32}H_{49}ONBr$: N, 2.58; Br, 14.76. Found: N, 2.49; Br, 14.98.

III. Five grams of dibromocholestanone is heated with 50 cc. of dimethylaniline for five hours. The reaction mixture is treated as in Expt. I. After evaporation of the ether, a dark-brown colored oil remains to which was added a small amount of alcohol. By standing for several days in the ice-box, a small amount of crystals came out, the main part being a brown oil. As it was too difficult to separate the crystals, the mixture was taken up with ethyl acetate and alcohol added. Light brown flakes precipitated which were filtered and recrystallized four times from ethyl acetate and alcohol, finally from ethyl acetate: 50 mg. of white needles was obtained, melting point 230–232°.

Calcd. for $C_{33}H_{47}N$: C, 86.65; H, 10.27; N, 3.08. $C_{34}H_{49}N$: C, 86.63; H, 10.40; N, 2.97. $C_{35}H_{53}N$: C, 86.24; H, 10.87; N, 2.87. Found: C, 86.63; H, 10.37; N, 3.13.

A small amount of the substance was dissolved in alcohol and several drops of acetic acid added. After further addition of a solution of *p*-nitrodiazobenzene a deep wine-red coloration was obtained.

RESEARCH LABORATORY
SCHERING CORPORATION
BLOOMFIELD, N. J.

RECEIVED MARCH 12, 1937

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[3] We have also carried out experiments in which potassium acetate was used for the removal of the bromine. These experiments were made in acetic acid, ethyl alcohol, butyl alcohol and dioxane as solvents. Our results agree only partly with Butenandt *et al.*[1c] so that further investigation of these reactions seems necessary. Potassium phenolate gave a substance which coupled with *p*-nitrodiazobenzene in alkaline solution to give a deep bluish-red. This substance may also be a derivative of a diphenyl-like combination of the phenol with the cholestanone.

[4] Doré and Petrow, *J. Chem. Soc.*, 1392 (1935).

Synthesis of *d,l*-Alanine in Improved Yield from α-Bromopropionic Acid and Aqueous Ammonia

BY WALTER C. TOBIE AND GILBERT B. AYRES

After having synthesized *d,l*-alanine by the excellent but tedious method of Kendall and McKenzie,[1] we decided to try to adapt the method of Orten and Hill[2] for glycine to making *d,l*-alanine from α-bromopropionic acid and aqueous ammonia.

The following method has been worked out and is giving satisfactory results. Pour slowly and with stirring, 100 g. (0.65 mole) of cold (1–4°) α-bromopropionic acid (Eastman No. 981) into 3 liters (44.5 moles) of cold (1–4°) concentrated aqueous ammonia (sp. gr. 0.90) in a glass-stoppered bottle. Allow the mixture to stand at room temperature (below 40°) for at least four days. Evaporate under reduced pressure on a steam-bath to about 300 cc. Filter and evaporate to about 200 cc., cool, add 1 liter of methanol and cool overnight at 1–4°. Filter off the crystals of *d,l*-alanine and wash with methanol and ether; yield 42–46 g., 72–79% of theoretical. Recrystallize the crude product by dissolving in 200 cc. of hot water and by adding 1 liter of methanol, cooling and washing as before; yield 38–40 g., 65–68% of theoretical. This product is bromide free and contains only small amounts of ammonia which may be removed by using Permutit on the second crystallization or recrystallizing a third time. The purified product has a melting point of 194–195° dec., and contains 15.79% nitrogen (same as theoretical).

Other syntheses were carried out in the cold (1–4°) but this did not affect the yield. A temperature above 40° reduced the yield. A reaction time of less than four days cut down the yield, whereas a time of more than four days did not increase the yield. α-Chloropropionic acid gave poorer yields (43–46% of the theoretical) than the α-bromo acid.

CONTRIBUTION NO. 88 FROM
DEPARTMENT OF BIOLOGY AND PUBLIC HEALTH
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.

RECEIVED FEBRUARY 26, 1937

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[1] Kendall and McKenzie, *Org. Syntheses*, **9**, 4 (1929).

[2] Orten and Hill, THIS JOURNAL, **53**, 2797 (1931).

COMMUNICATIONS TO THE EDITOR

REACTIONS OF CYCLOHEXANONE WITH DIAZOETHANE

Sir:

It has been shown by Mosettig and Burger [This Journal, **52,** 3456 (1930)] and by Meerwein (German Patent 579,309) that cyclohexanone reacts with diazomethane to form cycloheptanone and cycloöctanone as main products. The reaction takes place slowly even in the presence of a catalyst. Mosettig and Burger have suggested the possibility of replacing diazomethane by diazoethane and its homologs in this reaction.

In an investigation of the reactions of cyclic ketones with diazomethane and similar compounds which is under way in this Laboratory, the reaction of cyclohexanone with diazoethane has been carried out and the product obtained proved to be α-methylcycloheptanone. It was identified as the semicarbazone, m. p. 128–129°. Isolation of the product was brought about by removing the unattacked cyclohexanone with bisulfite solution, methylcycloheptanone being unaffected by this reagent. In contrast to the reaction with diazomethane, diazoethane requires no catalytic influence and the reaction is completed in a much shorter period of time. The reaction with diazomethane requires several days for completion while that with diazoethane takes less than twenty-four hours.

It is interesting further to record that while diazomethane reacts readily with cyclohexanone to form both cycloheptanone and cycloöctanone, according to the conditions of the reaction, it is without effect on cycloheptanone and reacts to a slight extent only with cyclopentanone, the products being mainly cycloheptanone together with a small amount of cyclohexanone.

In order to obtain information on the behavior of substituted cyclic ketones toward diazomethane and diazoethane reactions have been carried out with α-chlorocyclohexanone. Diazomethane gave practically a quantitative yield of α-chlorocycloheptanone while diazoethane gave methylchlorocycloheptanone as the main product.

These reactions were carried out in ether solution. The ketone was added to the ethereal solution of diazomethane or diazoethane and if evolution of nitrogen did not occur immediately methyl alcohol was added to catalyze the reaction. Completion of the reaction was indicated by disappearance of the yellow color in the solution.

Chemical Laboratories
Clark University
Worcester, Mass.

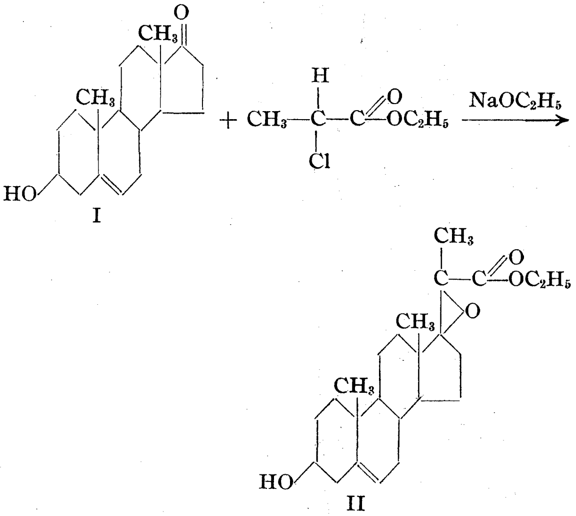
Albert P. Giraitis
Jesse L. Bullock

Received March 26, 1937

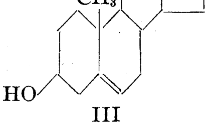
THE CONDENSATION OF DEHYDROANDROSTERONE WITH ETHYL α-CHLOROPROPIONATE

Sir:

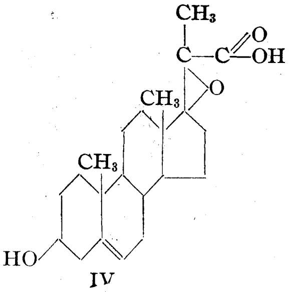
In the course of certain studies on the chemical properties of dehydroandrosterone, I, we have observed that under suitable conditions, in the presence of sodium ethylate, it is possible to effect a condensation of the Darzens type [*Compt. rend.*, **141,** 766 (1906)] between this hormone and ethyl α-chloropropionate according to the scheme



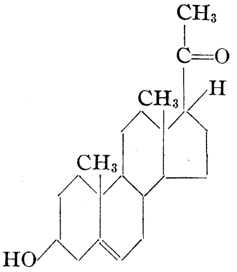
Some androstenediol-(3,17), III, is also formed during the reaction by the reducing action of the sodium ethylate. We have also found that hydrolysis of the ester oxide, II, with sodium hy-



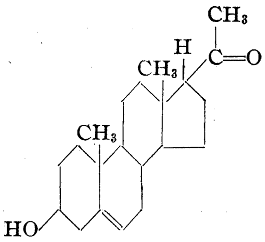
III



IV



V



VI

droxide yields two products: (a) an acid which forms an insoluble sodium salt, and presumably has the formula IV; and (b) a mixture of ketones formed by a rearrangement process having properties of Δ^5-pregnenolone, V, and Δ^5-*iso*-pregnenolone, VI, previously prepared from stigmasterol and pregnanediol by Fernholz [*Ber.*, **67,** 1855, 2027 (1934)] and by Butenandt and his co-workers [*Ber.*, **67,** 1611, 1901 (1934); **70,** 96 (1937)]. The exact proportions of the two ketones in the mixture are now being investigated, and experimental studies on the rearrangement of the acid, IV, into the corresponding ketones are in progress. The details of our experimental results will be published in a forthcoming paper. We hope that this announcement may serve as a reservation of this research project.

FRICK CHEMICAL LABORATORY
PRINCETON, NEW JERSEY
WILLIS A. YARNALL
EVERETT S. WALLIS

RECEIVED APRIL 1, 1937

NEW BOOKS

Alchemy and Other Chemical Achievements of the Ancient Orient. The Civilization of Japan and China in Early Times as Seen from the Chemical Point of View. By Dr. MASUMI CHIKASHIGE, Emeritus Professor of Kyoto Imperial University. Rokakuho Uchida, Tokyo, Japan, 1936. 102 pp. 17 plates. 12.7 × 18.8 cm. Price, 1.50 Yen.

This is an English translation of a book which appeared in the Japanese language in 1929 under a title which may properly be translated "Metallurgic Arts in the Orient." The Japanese version contained a discussion of European alchemy which is omitted from the present translation. The work is divided into three parts which deal, respectively, with Chinese alchemy, with Chinese bronze and with Japanese steel swords.

The author considers that many alchemical books can be enumerated, but that "in the final analysis, only two works, *Pao-p'u-tzu* (written by *Ko Hung,* fourth century A.D.) and *Pên Ts'ao Ching*" (a treatise on materia medica published toward the end of the *Han* dynasty) "remain as the authentic sources of information on the earlier Chinese alchemy." Biographical accounts of *Ko Hung* and *T'ao Hung-ching* are given, and many interesting quotations from the second (*Lun Hsien,* "Essay on the Immortals"), the fourth (*Chin Tan,* "Gold Medicine"), the eleventh (*Hsien Yao,* "Medicines of the Immortals") and the sixteenth (*Huang Pao,* "The Yellow and the White") of the Inner Chapters of "*Pao-p'u-tzŭ.*" Chikashige discusses the identity of some of the materials which *Ko Hung* used, and concludes that some of the processes may actually have yielded real gold because of the gold which existed in small amounts in the reagents.

The discussion of ancient Chinese bronzes centers around the "Six Recipes of *Chin*" which are set down in the *Chou Li K'ao Kung Chi* (Artificers' Record, the sixth part of the *Chou* ritual) which was published during the *Chou* dynasty in the tenth century B.C. The author concludes that these recipes, except the last one, are reasonable. He discusses the properties of the several kinds of bronze which correspond to them, and finally reports chemical analyses of ancient bronzes in which the proportions of copper to tin agree with those laid down in certain of the recipes. He has wisely made his analyses upon the uncleaned bronze objects, determining the total amount of each metal present in the combined mass of metal and oxidized material.

"As to the method of forging swords in extreme antiquity, no history nor tradition has been handed down; but some of the straight swords excavated by archeologists were once submitted to investigation from which it may be concluded with some justice that they belong to the class of forged swords. For they showed some signs of having been forged by 'folding,' or even by 'combining' different sorts of iron. The art of forging made great progress when in the days of the Prince Regent *Shōtoku* (573–621) it was taught by some naturalized smiths at Oshinumi and later when Emperor *Gotoba* (1180–1239) gave directions to the noted smiths of the various provinces and made them forge at the court. All this concerns the method of forging the so-called *kotō* (old swords) but this method was lost during the age of civil wars toward the end of the *Ashikaga* Period. *Shintō* (new swords) made their first appearance toward the beginning of the *Tokugawa* Period and during the *Anei* (1772–1780) era or thereabouts *shinshintō* (new new swords) began to be turned out. A sword-smith, named *Suishinshi* is said to have been the originator of the *shinshintō* school. He was a diligent investigator of the oldest school of sword forging, and thus the once obscured method became clear again; but it did not live long as such, for *Suishinshi* improved it further and gave birth to a new school. The doctrine of the school of *shinshintō* still survives among the sword-smiths of the last days of the *Tokugawa* Period."

Chikashige describes the methods of the *shinshintō* school, having procured his information from the notes of two who were instructed by master sword-smiths. The descriptions are clearly illustrated by diagrams, and the effect of the process upon the structure of the metal is made evident by micrographs of cross sections. Micrographs of cross sections of ancient Japanese swords and of inferior swords from Java and Formosa show plainly the manner in which they were forged.

TENNEY L. DAVIS

Boden und Pflanze. (**Soil and Plant**). By Sir E. JOHN RUSSELL. Second edition. Translated from the 6th English edition by Dr. K. W. MÜLLER, Zurich. Foreword by Prof. Dr. GEORG WIEGNER. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1936. xiii + 446 pp. 60 figs. 16 × 24 cm. Price, RM. 30; bound, RM. 32.

The contributions of Sir John Russell rank high in international soil science and this German translation of the sixth edition of his Soil Conditions and Plant Growth is especially interesting at this time. The first German edition appeared in 1914 and was by Hans Brehm. This second edition is by K. W. Müller of Zurich, and the late Prof. G. Wiegner has supplied the book with an appreciative preface. This new German edition meets all expectations and has in contrast with the first many changes to show, the contents having risen from 243 to 446 pages, and also the arrangement of the material has been considerably altered. The translation is well handled with a fine appreciation of technical accuracy. The following chapter headings give a good idea of the scope of the book: historical introduction; the influence of the soil on the growth of plants; the composition of the soil; the soil in nature; the changes in its mineral composition; the changes in organic matter; the micro flora of the soil and its relation to plant growth; the biological relationships in the soil; soil and plant; method of evaluating soil; methods of soil analysis. The author has handled the material in a different manner from that customary in most soil books. The soil itself and its relation to the plant receives the most detailed and thorough consideration. Even the first edition of the book received much praise in Germany and this second edition is considered as a most welcome corollary to German textbooks on Soil Science, as the name of its distinguished author is a guarantee of its value to soil science internationally everywhere.

OSWALD SCHREINER

Essential Principles of Organic Chemistry. By CHARLES S. GIBSON, O.B.E., M.A., Sc.D., F.R.S., Professor of Chemistry in the University of London, at Guy's Hospital Medical School. Cambridge University Press; The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1936. viii + 548 pp. 14.5 × 22.5 cm. Price, $5.00.

This text is designed for use in teaching organic chemistry to students who expect to specialize in the subject, and others for whom a thorough understanding of the principles of the science is essential. An examination of the contents leaves no doubt that the book is well suited to the group for which it is intended.

The first two pages form a very attractive introduction involving the presentation of the "carbon skeletons" of many compounds; ethyl ether, isoquinoline, diphenylmercury and trimethylamine are some of the examples. Then follows a description of analytical methods. While this latter material provides the logical and classical approach to the subject, it will seem to some a trifle old-fashioned compared with the introductory subject matter of the better American texts.

The first chapter deals with the aliphatic hydrocarbons, and the second with aromatic hydrocarbons. From this point, aliphatic and aromatic compounds are treated together. The result is very satisfactory. The presentation is excellent throughout.

The only serious adverse criticism of the book would be that many of the recent important developments are ignored. Synthetic plastics, polymerization, the synthesis of alcohols from olefins, ethylene glycol and its derivatives, the formation of phenol and aniline directly from chlorobenzene, dyes and terpenes are topics which are treated very briefly or omitted entirely.

The sections devoted to carbohydrates, purines, the Beckmann rearrangement and crystal structure are particularly satisfactory.

The book is well printed, is plentifully supplied with clear, attractive formulas and has very few typographical errors. It is to be highly recommended to teachers, with the reservation that the material needs to be supplemented with reference to certain of the newer developments.

REYNOLD C. FUSON

Die chromatographische Adsorptionsmethode, Grundlagen, Methodik, Anwendung. (**The Chromatographic Adsorption Method: Principles, Procedures and Applications.**) By Dr. L. ZECHMEISTER, Professor, and Dr. L. v. CHOLNOKY, Lecturer, at the Chemical Institute of the University of Pécs (Ungarn). Verlag von Julius Springer, Schottengasse 4, Wien I, Austria, 1937. xi + 231 pp. 45 figs. 14 × 21 cm. Price, RM. 14.40.

This carefully printed publication is an excellent compendium of the improvements and applications of the Tswett chromatographic adsorption method. The various uses of this columnar adsorption method for the detection, separation, isolation, purification and identification of chemical compounds are discussed. Consideration is given to the relation between the chemical structure and the adsorbability of organic compounds. Descriptions of the adsorbents and of the solvents required for the adsorption and elution of the compounds are included. The preparation of the adsorption columns is described, and methods for following the separation of colorless substances upon the columns are illustrated. The greater part of the volume (pp. 76–191) is devoted to the description of the separation of specific substances which are classified according to groups: (a) natural pigments, such as chlorophylls and derivatives, bile pigments, carotenoids and derivatives, naphthoquinone and anthraquinone pigments, flavines, pterine, anthrocyanins and other pigments; (b) synthetic dyes; (c) colorless substances, such as aliphatic and aromatic hydrocarbons and derivatives, polycyclic compounds, sterols, alkaloids, enzymes, vitamins, hormones, tannins and drugs. Photographs illustrating the separation of pigments by adsorption upon columns are reproduced. A comprehensive bibliography (all titles in German) and author and subject indexes are appended.

Everyone who is concerned with the isolation and identification of chemical compounds should find many helpful suggestions in this publication. Experience has shown, however, that the adsorptive properties of different preparations of the same adsorbent may vary more than is indicated; hence, familiarity with the properties of the adsorbents becomes an important factor in the application of the chromatographic adsorption technique.

HAROLD H. STRAIN

BOOKS RECEIVED

March 15, 1937–April 15, 1937

JEROME ALEXANDER. "Colloid Chemistry. Principles and Applications." Fourth edition. D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 505 pp. $4.50.

J. F. BARKLEY. "Questions and Answers on Boiler Feed Water Conditioning." U. S. Bureau of Mines. Superintendent of Documents, Government Printing Office, Washington, D. C. 121 pp. $0.20.

J. DUCLAUX. "Diffusion. VI. Dans les Liquides. VII. Dans les Gels et les Solides." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris, France. 90 + 50 pp. 20 + 12 fr.

L. EBERLEIN. "Die neueren Milchindustrien." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 135 pp. RM. 5.50; bound, RM. 6.50.

RENÉ FABRE. "Toxiques Minéraux. IV. Phosphore, Acides et Alcalis. March Générale de l'Expertise." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris, France. 106 pp. 12 fr.

L. F. FIESER. "The Chemistry of the Natural Products Related to Phenanthrene." Second edition, with appendix. Reinhold Publishing Corporation, 330 West 42d St., New York, N. Y. 456 pp. $7.00.

LESLIE J. HARRIS. "Vitamins in Theory and Practice." Second edition. The Macmillan Company, 60 Fifth Ave., New York, N. Y. 242 pp. $3.00.

G. S. HARTLEY. "Aqueous Solutions of Paraffin-Chain Salts. A Study in Micelle Formation." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris, France. 69 pp. 15 fr.

ERICH HEYMANN. "The Sol-Gel Transformation." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris, France. 68 pp. 15 fr.

DOUGLAS G. HILL, JOHN H. SAYLOR, WARREN C. VOSBURGH and ROBERT N. WILSON. "Elementary Chemistry." Henry Holt and Co., 257 Fourth Ave., New York, N. Y. 473 pp. $2.80.

ERIC HOLMES. "The Metabolism of Living Tissues." The Macmillan Company, 60 Fifth Ave., New York, N. Y. 235 pp. $2.25.

GLENN L. JENKINS and ANDREW G. DUMEZ. "Quantitative Pharmaceutical Chemistry, Containing Theory and Practice of Quantitative Analysis Applied to Pharmacy." McGraw-Hill Book Co., Inc., 330 West 42d St., New York, N. Y. 466 pp. $3.50.

ALCIDE JOUNIAUX. "Volumétrie. I. Alcalimétrie. II. Acidimétrie. III. Argentométrie. IV. Manganométrie et Chromométrie. V. Iodométrie et Arsenométrie." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris, France. 60 + 30 + 26 + 44 + 50 pp. 12 + 8 + 8 + 10 + 12 fr.

ROBERT KREMANN and MAX PESTEMER. "Zusammenhänge zwischen Eigenschaften und chemischen Konstitution." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 225 pp. RM. 16; bound, RM. 18.

FRITZ LÖWE. "Atlas der Analysen-linien der wichtigsten Elemente." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 37 pp. RM. 10.

L. PIATTI. "Nachweis und Bestimmung von Lösungsmitteldämpfen." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 87 pp. RM. 6.50; bound, RM. 7.50.

N. V. SIDGWICK. "The Organic Chemistry of Nitrogen." Revised and rewritten by T. W. J. Taylor and Wilson Baker. Oxford University Press, 114 Fifth Ave., New York, N. Y. 590 pp. $8.50.

A. F. H. WARD. "Applied Chemistry for Engineers." Longmans, Green and Co., 114 Fifth Ave., New York, N. Y. 127 pp. $1.75.

FRANK C. WHITMORE. "Organic Chemistry." D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 1080 pp. $7.50.

"Zur Entwicklung der Chemie der Hochpolymeren Kunststoffe, Kautschuk, Anstrichmittel, Cellulosederivate." Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 214 pp. RM. 2.10.

"Structure and Molecular Forces in Pure Liquids and Solutions. A General Discussion." Published for the Faraday Society by Gurney and Jackson, 33 Paternoster Row, London, England. 282 pp. 13s./2d.

JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 59 JUNE 5, 1937 NUMBER 6

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

Photochemical Investigations. IV. The Photochemical Decomposition of Deutero-ammonia[1]

BY EDWIN O. WIIG

The photochemical decomposition of deutero-ammonia is of interest since it can be investigated at wave lengths which, although near one another in wave length, show different types of absorption. Both ammonia and deutero-ammonia show absorption beginning at about λ 2300 Å. and extending to shorter wave lengths.[2] In ammonia the bands are diffuse, but in the case of deutero-ammonia the principal band at λ 2136–39 Å. is discrete, while at about λ 2105–22 and λ 2065–80 Å. there are exclusively diffuse bands.[3] The latter ND_3 bands correspond to predissociation and the primary process should presumably be the same as in the similar ammonia bands, a dissociation into ND_2 and D. Absorption of light in the discrete band should result in the formation of an electronically excited molecule. The photochemical decomposition of deutero-ammonia in the bands at about λ 2136–39 and 2105–22 Å. might, therefore, proceed differently, although the energies involved are almost identical.

This paper presents the results of a study of the photolysis of deutero-ammonia by the zinc spark lines at λλ 2138 and 2100 Å., in the discrete and diffuse bands, respectively. In order to compare these results with those for ammonia, measurements of the quantum yield for the latter at λ 2100 Å. were also made in the same cell.

Experimental Details

The light source and apparatus were the same as those used in previous investigations dealing with ammonia.[4] As the two earlier cells were not available, use was made of a third cylindrical cell, Cell 3, 25 mm. in diameter and 100 mm. long, with plane parallel windows fused on the ends. The materials used, with the exception of the deutero-ammonia, were prepared as before. The corrections for the energy loss at the rear cell window at the two wave lengths investigated were obtained from photolysis of hydrogen bromide under conditions identical with those prevailing in the ammonia or deutero-ammonia decompositions. The data for the hydrogen bromide decompositions have been omitted since they are similar to earlier data.[4]

Results

The quantum efficiencies obtained in the decomposition of deutero-ammonia at λλ 2100 and 2138 Å. and of ammonia at λ 2100 Å. in Cell 3 at room temperatures (23–29°) are shown in Tables I, II and III, respectively. For purposes of comparison these data are plotted in Figs. 1 and 2. In the calculation of the quantum yields it was assumed that the products are $N_2 + 3D_2$ from analogy with the ammonia photodecomposition. The question of a change in composition of the gaseous products as their pressure is decreased has already been discussed.[4] In a number of preliminary experiments with deutero-ammonia good checks could not be obtained.

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[1] The results of this investigation were presented at the Rochester, N. Y., Intersectional meeting of the American Chemical Society, June 16–18, 1936.

[2] Dixon, *Phys. Rev.*, **43**, 711 (1933); Duncan, *ibid.*, **47**, 822, 886 (1935); **50**, 700 (1936).

[3] The present experiments were undertaken at the suggestion of Professor Hugh S. Taylor of Princeton University. The author is greatly indebted to Professor Taylor and Dr. W. S. Benedict for communicating to him the results of their study of the absorption spectrum of deutero-ammonia and for supplying a sample of pure ND_3.

[4] Wiig, THIS JOURNAL, **57**, 1559 (1935); **59**, 827 (1937).

This effect was eliminated by the following procedure. Deutero-ammonia at high pressure (500 mm.) was admitted to the cell (previously heated and evacuated, and cooled), the pressure reduced to 410 mm. and the quantum yield, ϕ, determined for λ 2100 and then λ 2138 Å. The pressure was again reduced to the next desired pressure, followed by a determination of ϕ for λ 2138 and then λ 2100 Å., and this procedure continued down to low pressures. Four samples of deutero-ammonia were used in this fashion in the experiments in Tables I and II. Exclusive of the preliminary runs, a total of 81 experiments, including checking the apparatus against hydrogen bromide, were performed. Of these only two have been omitted from the tables, both being rejected because of experimental difficulties.

TABLE I

PHOTOLYSIS OF DEUTERO-AMMONIA IN CELL 3

λ 2100 Å. Volume, 228 cc.

P_{ND_3}, mm.	Exposure, sec.	Quanta absorbed $\times 10^{-14}$	$P_{N_2+D_2}$, microns	Quantum yield
2	1800	219	0.34	0.059
5	1440	294	.49	.063
20	1200	516	2.00	.147
30	1500	886	4.12	.176
34	1200	826	4.79	.221
35	1440	929	5.19	.216
50	900	620	3.17	.193
65	1260	716	4.12	.209
82	900	620	3.47	.213
92	900	862	4.83	.213
100	960	766	4.12	.204
120	1020	844	4.53	.204
145	1380	1026	5.27	.196
146	900	786	4.49	.217
180	1440	1439	7.49	.199
201	900	877	4.20	.182
253	1200	1521	6.75	.168
300	900	840	3.64	.164
340	1260	1740	7.34	.160
375	900	747	2.84	.144
410	1200	1992	7.44	.142
430	1320	1194	4.49	.141

TABLE II

PHOTOLYSIS OF DEUTERO-AMMONIA IN CELL 3

λ 2137 Å. Volume, 228 cc.

P_{ND_3}, mm.	Exposure, sec.	Quanta absorbed $\times 10^{-14}$	$P_{N_2+D_2}$, microns	Quantum yield
2	2040	54	0.13	0.109
5	1740	78	.19	.114
20	1560	224	1.12	.190
30	1740	328	1.64	.191
35	1560	434	2.76	.239
50	1560	247	1.53	.230
64	1500	471	3.34	.271
82	1680	326	2.23	.258
92	1500	337	2.37	.266
100	1500	277	1.80	.245
120	1320	338	2.50	.281
146	1800	447	3.12	.264
180	1800	571	3.44	.230
200	1200	318	1.53	.183
200	1260	301	1.75	.223
200	1200	291	1.71	.225
253	1680	517	2.84	.209
253	2040	308	2.00	.247
255	1260	439	2.61	.225
300	1200	385	2.23	.222
345	1260	478	2.72	.216
370	1200	294	1.75	.226
413	1200	460	2.15	.177
430	1200	405	2.10	.196

TABLE III

PHOTOLYSIS OF AMMONIA IN CELL 3

λ 2100 Å. Volume, 228 cc.

P_{NH_3}, mm.	Exposure, sec.	Quanta absorbed $\times 10^{-14}$	$P_{N_2+H_2}$, microns	Quantum yield
1	1800	194	0.38	0.074
8	1200	736	1.51	.078
21	1200	879	4.49	.194
29	2040	1610	8.49	.199
41	4860	3750	22.48	.247
41	1800	787	4.78	.252
45	1260	1050	7.78	.280
60	900	929	7.06	.291
60	900	661	4.87	.279
81	960	777	6.55	.319
83	900	944	7.49	.303
98	960	997	7.11	.272
106	900	894	7.11	.302
117	960	843	5.89	.266
149	900	826	5.43	.247
193	900	762	4.87	.242
232	900	838	5.03	.227
235	1020	964	6.51	.259
267	900	838	4.79	.216
320	960	947	5.19	.207
335	960	930	5.15	.209
417	900	832	4.72	.214
442	900	730	3.70	.192

Discussion

It will be seen from Fig. 1 that, at the same wave length (λ 2100 Å.) and for the same type of absorption, the decomposition proceeds about 1.3–1.5 times as rapidly with ammonia as with deutero-ammonia. This is apparently in disagreement with the results of Melville,[5] who reports NH_3 to ND_3 ratios of 2.6, 2.3 and 2.6 to 1. These ratios were obtained with 2.0 cm. length of ammonia and of deutero-ammonia, respectively, at pressures of 100 mm. exposed to a quartz mercury arc. The mercury lines around λ 2100 Å. were effective in these experiments,

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(5) Melville, *Proc. Roy. Soc.* (London), **A152**, 325 (1935).

since absorption by NH_3 and ND_3 increases with decrease in wave length. Under his condition, Melville states, the absorption by NH_3 is about 96% for light around λ 2100 Å. and, presumably, absorption by ND_3 would differ only slightly from this. Calculations from actual measurements made in this Laboratory on 3.5 cm. of NH_3 at 100 mm. pressure indicate for a 2.0 cm. path 88% absorption with monochromatic light of λ 2100 Å., in fair agreement with the above 96%. But absorption by ND_3 of λ 2100 Å. is considerably weaker. From measurements on 10.0 cm. of ND_3 at 100 mm. pressure the absorption for a length of 2.0 cm. is calculated to be only 40% instead of the 88% obtained with NH_3. Thus Melville's ratios are much too high and the disagreement vanishes when allowance is made for the different absorptions.

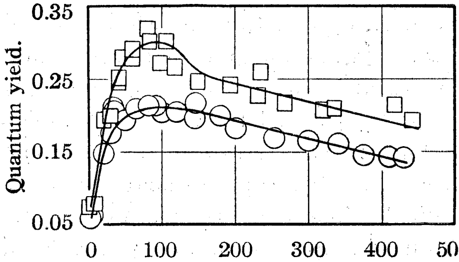

Fig. 1.—A comparison of the quantum yields for ammonia, □; and deutero-ammonia, ○, at λ 2100 Å.

The same sort of pressure dependence of the quantum yield as has previously been found[4] for ammonia is shown by deutero-ammonia (Fig. 1). This indicates that the mechanisms of the reactions following the primary process are similar. At λ 2100 Å. ND_3 and NH_3 show the same type of absorption,[3] so that the mechanism suggested for NH_3 should be applicable to ND_3. Melville[5] has shown that NH_3 and ND_3 are inhibited about equally by both hydrogen and deuterium atoms. It follows from the reactions suggested for the NH_3 decomposition[4] that the smaller yields with ND_3 are due to the reaction

$$ND_2 + ND_2 \longrightarrow N_2 + 2D_2$$

being slower than the corresponding one involving hydrogen. This suggestion has already been made by Melville and, as he points out, this is in keeping with previous experience in the kinetics of hydrogen and deuterium compounds.

The greater quantum yield for ND_3 with λ 2138 Å. as compared with λ 2100 Å. (Fig. 2) is rather puzzling. Offhand, most investigators would probably guess just the opposite, although a similar result has been found by West and Ginsburg[6] in the photolysis of gaseous ethyl iodide in the regions of continuous and banded absorption. In the photodecomposition of acetaldehyde Leighton and Blacet[7] found a higher yield in the region of fine structured bands as compared with the diffuse bands but they were able to show that the mercury line absorbed in the former region fell directly between two band maxima and the absorption was really due to the underlying continuum. In the case of deutero-ammonia there is no such underlying continuum, λ 2138 Å. falling in the discrete band at λ 2136–39 Å. The similarity in the pressure dependence of the yields at λλ 2138 and 2100 Å. indicates a

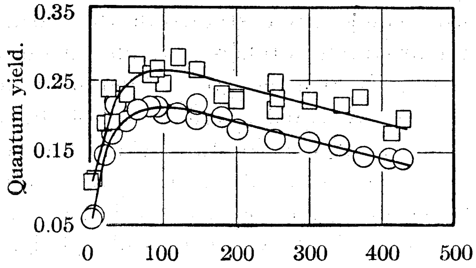

Fig. 2.—A comparison of the quantum yields for deutero-ammonia at λ 2138 Å., □; and λ 2100 Å., ○.

similarity in the mechanisms and suggests that at λ 2138 Å. we have

$$ND_3 + h\nu \longrightarrow ND_3' \qquad (1)$$

$$ND_3' + ND_3 \longrightarrow ND_2 + D + ND_3 \qquad (2)$$

The greater yield at λ 2138 Å. can then readily be accounted for by supposing that a small proportion of the collisions of electronically excited molecules, ND_3', with normal molecules, reaction (2), results in

$$ND_3' + ND_3 \longrightarrow N_2 + 3D_2 \qquad (3)$$

This would lead to a constant difference in the yields down to pressures where the reaction becomes heterogeneous,[4] in agreement with experiment. A somewhat similar suggestion has been made by West and Ginsburg and by Rollefson.[8] The homogeneous bimolecular decomposition of ammonia would probably require an activation energy greater than about 80 kcal.,[9] which is

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[6] West and Ginsburg, THIS JOURNAL, **56**, 2626 (1934).

[7] Leighton and Blacet, *ibid.*, **55**, 1766 (1933).

[8] Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

[9] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, London, 1933, p. 365.

considerably less than the 135 kcal. supplied by one einstein at λ 2138 Å.

Summary

The photodecomposition of ammonia is found to proceed about 1.3–1.5 times as rapidly as that of deutero-ammonia in the predissociation bands at λ 2100 Å. Approximately the same ratio holds for the rate of decomposition of deutero-ammonia at λ 2138 Å. in a discrete band to that at λ 2100 Å. in a diffuse band. These differences in rates are discussed and explanations to account for them suggested.

ROCHESTER, NEW YORK RECEIVED MARCH 23, 1937

[CONTRIBUTION FROM THE HENRY PHIPPS INSTITUTE OF THE UNIVERSITY OF PENNSYLVANIA]

The Chemical Composition of the Active Principle of Tuberculin. XX. Comparative Study of the Yield, Potency, Specificity and Acid–Base-Combining Capacities of the Proteins from Five Human Tubercle Bacilli Culture Filtrates and other Acid-Fast Bacilli

BY FLORENCE B. SEIBERT[1]

During comparative studies of the chemistry of different strains of tubercle bacilli, the question has arisen whether as great differences might not occur on repeated examinations of the same strain. It is also a question whether constant differences can be established between tubercle bacilli and other members of the large group of acid fast bacteria, to which the tubercle bacillus belongs. In addition to the well-known method of differentiating the human, bovine and avian types of tubercle bacilli by means of their respective virulences for different animals, the distinctions made by Wilson[2] on the basis of agglutination and by Furth[3] on the basis of complement fixation and absorption experiments, it has recently been possible to differentiate them by means of the serological precipitin reaction,[4] using the purified proteins isolated from the bacillary culture filtrates as antigens. Furthermore, the proteins from these three types of tubercle bacilli, as well as from the acid-fast bacillus found on timothy grass, differed quantitatively in potency when equal doses were injected in the skin of tuberculous animals,[5] whereas no difference whatever could be distinguished between the potencies of proteins prepared from three different strains of the human type tubercle bacilli which differed widely in their virulence.

Chemical differences in the lipide contents of the different types of tubercle bacilli, human, bovine, avian, and the acid-fast timothy bacillus have been reported by Anderson[6] and his coworkers, and Chargaff and Dieryck.[7] Anderson noted especially the presence of an optically active liquid saturated fatty acid, phthioic acid, in the human H37 strain, whereas analogous acids from the other types of acid-fast organisms were optically inactive. He has made a further report[8] on the lipide contents of the bacilli of four different cultures of tubercle bacilli, recently isolated from human cases of tuberculosis, in comparison with results obtained on a freshly grown lot of the human type H37 bacillus.

The following paper is a comparative study of the proteins isolated from the culture filtrates of the same five batches of human tubercle bacilli used in Anderson's[8] studies. The results will be compared with similar studies on comparable proteins prepared from the bovine and avian tubercle bacilli and leprosy and timothy grass acid-fast organisms.

Experimental

History of Strains of Human Tubercle Bacilli Used.—

Strain A10—isolated May, 1932, on guinea pig passage from retroperitoneal lymph glands of patient (25435). Pathogenic for guinea pigs and only very slightly for rabbits. Recent test showed no pathogenicity for rabbits.

Strain A12—isolated November, 1932, from the sputum of patient (38135). Pathogenic for guinea pigs; nonpathogenic for rabbits.

Strain A13—isolated December, 1932, from the sputum of

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(1) Aided by a grant from the Committee on Medical Research of the National Tuberculosis Association.

(2) G. S. Wilson, *J. Path. Bact.*, **28**, 1, 69 (1925).

(3) J. Furth, *J. Immunol.*, **12**, 273 (1926).

(4) F. B. Seibert, *Am. Rev. Tuberc.*, **21**, 370 (1930).

(5) F. B. Seibert and N. Morley, *J. Immunol.*, **24**, 149 (1933).

(6) R. J. Anderson, *Physiol. Rev.*, **12**, 166 (1932).

(7) E. Chargaff and J. Dieryck, *Biochem. Z.*, **255**, 319 (1932).

(8) J. A. Crowder, F. M. Stodola, M. C. Pangborn and R. J. Anderson, THIS JOURNAL, **58**, 636 (1936).

patient (21443). Mildly pathogenic for guinea pigs; non-pathogenic for rabbits.

Strain A14—isolated January, 1933, from the sputum of patient (38502). Pathogenic for guinea pigs; non-pathogenic for rabbits.

H37—(Saranac Lake strain isolated in 1910.)[9] Non-pathogenic for rabbits when recently tested.

The first four strains were isolated at the Henry Phipps Institute by J. D. Aronson and H. J. Henderson.

Isolation of Proteins.—Approximately 300 cultures of each strain were grown in 1-liter Pyrex bottles under identical conditions on Long's synthetic medium[10] for eight weeks during 1934, by Mr. John Glenn of the Mulford Biological Laboratories, Sharp and Dohme, Glenolden, Pa. The bacterial masses were then filtered off on Büchner funnels and subsequently used by Dr. Anderson. The filtrates were preserved with 0.5% phenol, later filtered free of bacteria on Mandler filters, and sent to our laboratory in 8-liter Pyrex bottles. The quantities of raw tuberculin so prepared varied from 32 to 44 liters per strain, representing from 53 to 60 liters of original medium.

The proteins were isolated from these filtrates by a method described in 1932.[11] Briefly it was as follows. The unheated culture filtrates were concentrated by means of ultrafiltration through alundum filters impregnated with 13% guncotton, and then washed free of filtrable substances by repeated additions of 0.5% phenol. The non-filtrable residue representing approximately a 100 times concentration of the original solution, was filtered through the Seitz filter and then precipitated with 10% trichloroacetic acid, washed on the centrifuge five to six times with trichloroacetic acid, partially dried *in vacuo* at room temperature and finally thoroughly extracted and dried to a powder, by grinding with anhydrous ether.

Analyses and Potency of the Proteins.—These powders designated as TPT-H37, TPT-A10, TPT-A12, TPT-A13 and TPT-A14, were then analyzed for ash and volatile substances at 110° by the micro methods described by Pregl[12] and for nitrogen by the Parnas–Wagner modification of the micro-kjeldahl method,[12] using selenium[13] instead of copper sulfate as the oxidizing agent.

The potencies of the products were compared by making six simultaneous injections, each of 0.1-cc. saline solution containing 0.005 mg. protein, in eleven tuberculous guinea pigs inoculated six weeks previously with 0.1 mg. of H37 bacilli. The five proteins were compared with an equal dose of Purified Protein Derivative[14] which is the standard purified tuberculin adopted by the National Tuberculosis Association.

The results of the analyses and potency tests are recorded in Table I. The constancy in the yield of protein from the five strains is remarkable, when consideration is given to the fact that the A13 strain grew sparsely and was found by Anderson[8] to have yielded the lowest bacterial mass per culture. The A10 protein proved to be much less soluble than any of the other proteins and consequently there was an obvious loss in the product during its isolation. There was comparatively little difference in the potencies of the five proteins, although the A10 and H37 were slightly less potent than the other three. All were less potent than the standard Purified Protein Derivative.

TABLE I

TPT made from strain of human tubercle bacillus	Yield, g. TPT per liter original medium	Moisture, %	Ash, %	Nitrogen (ash-free dry wt.), %	Potency, av. size skin reaction with 0.005 mg. tested simultaneously on 11 tuberculous guinea pigs, 48 hrs.
H37	0.30[a]	14.6		15.9	
	.26	9.5	1.3	15.2	14 × 16 × 2.7
A10	.18	4.7	0.9	14.2	13 × 15 × 2.9
A12	.24	9.0	.5	14.0	16 × 19 × 3.6
A13	.17	10.7	.4	13.9	16 × 18 × 3.2
A14	.24	8.8	.9	14.1	17 × 19 × 3.1

[a] This product was made in 1932 from the same H37 strain.

Serological Specificity of the Proteins.—Since no significant differences between the proteins were obtained by means of the preliminary analyses reported above, the very delicate serological precipitin reaction was employed. It has been shown by many investigators, but especially by Landsteiner,[15] that very small differences in chemical structure of proteins and even polypeptides can be detected by this method. Since earlier work[4] showed that proteins made similarly from different types of tubercle bacilli, human, bovine, avian and timothy grass, could be differentiated by means of the precipitin reaction, it was advisable to determine whether serological differences could also be detected between these five strains, all of the human type tubercle bacillus.

Five per cent. solutions of the different antigens were prepared by putting the powders into solution with the minimal amount of normal sodium hydroxide, neutralizing to litmus with 0.1 normal hydrochloric acid, and diluting to standard volume with saline containing 0.5% phenol.

Two rabbits were injected intracutaneously with 10 mg. of each antigen ten times at approximately weekly intervals. The increasing degree of sensitiveness of the animals was followed by observing the Arthus reactions which occurred, and seven days after the tenth injection the rabbits were bled to death. The precipitin tests were performed by adding to 12 tubes containing 0.1 cc. each of serum 0.1 cc. of varying dilutions of 1% antigen solutions, varying from 1:200 to 1:2,000,000. They were shaken and kept in the ice box for forty-eight hours and then the amount of precipitate in each tube was noted. A control tube with saline was negative in all cases.

Table II shows the results of these tests. No differences in serological specificity could be detected between the five human strains, H37, A10, A12, A13 and A14, either in the end titer or in the amount of precipitate in any of the tubes. On the other hand, differences could be detected between these human strain proteins and the proteins of

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(9) E. R. Baldwin, *J. Exptl. Med.*, **22**, 323 (1910).

(10) E. R. Long, *Am. Rev. Tuberc.*, **13**, 393 (1926).

(11) F. B. Seibert and B. Munday, *Am. Rev. Tuberc.*, **25**, 724 (1932).

(12) F. Pregl, "Quantitative Organic Microanalysis," 2d edition, Blakiston's Son and Co., 1930.

(13) J. Tennant, H. L. Harrell and A. Stull, *Ind. Eng. Chem., Anal. Ed.*, **4**, 410 (1932).

(14) F. B. Seibert, J. D. Aronson, J. Reichel, L. T. Clark and E. R. Long, *Am. Rev. Tuberc.*, supplement 30, 707 (1934).

(15) K. Landsteiner, "The Specificity of Serological Reactions," Charles C. Thomas, 1936.

TABLE II

PRECIPITIN TITERS WITH ANTIGENS

Immune anti-sera from rabbits in duplicate sensitized with	H37	A10	A12	A13	A14	Bovine	Timothy	Polysaccharide from human tubercle bacilli
TPT-H37	100 000	100 000	100 000	100 000	100 000	500 000[a]	20 000[a]	0
	100 000	100 000	100 000	100 000	100 000	500 000[a]	10 000[a]	0
TPT-A10	100 000	100 000	100 000	100 000	100 000	100 000[a]	0	0
	100 000	100 000	100 000	100 000	100 000	50 000[a]	0	0
TPT-A12	100 000	100 000	100 000	100 000	100 000	100 000	20 000[a]	0
	100 000	100 000	100 000	100 000	500 000	20 000[a]	50 000[a]	0
TPT-A13	100 000	100 000	100 000	100 000	100 000	100 000[a]	20 000[a]	0
	100 000	100 000	100 000	100 000	100 000	400[a]	5 000[a]	0
TPT-A14	100 000	100 000	100 000	100 000	100 000	50 000[a]	20 000[a]	0
	500 000	100 000	100 000	100 000	100 000	50 000[a]	20 000[a]	0
TPT-Bovine	100 000	50 000	100 000	50 000	100 000	100 000	0	0
	100 000	20 000	50 000	50 000	50 000	100 000	0	0
TPT-Timothy	50 000[a]	0	0	0	0	0	100 000	0
	20 000[a]	1 000[a]	200[a]	0	20 000[a]	0	100 000	0

[a] Precipitate light.

bovine or timothy bacilli. While the bovine antigen gave in all cases some precipitate with the five human type antisera and even in several cases, as high a titer, the amount of precipitate produced was always obviously less, and in many cases there was zoning effect. On the other hand, the bovine antisera gave as high titers and as heavy precipitates with the five human type antigens as with itself. The sparseness of precipitate was very conspicuous in the case of the timothy antisera precipitated with the human type antigens as well as with the different human type antisera precipitated with timothy antigen. Therefore, the timothy protein showed a high degree of specificity, as noted earlier,[4] the bovine protein some degree of specificity and the human proteins only a type specificity. While the similarities and differences here described were plainly seen on observing the tubes, there is no doubt that it will be possible to record such differences more nearly quantitatively when Heidelberger's[16] quantitative precipitin method is perfected so that it can be applied to bacterial proteins as well as to such proteins as have been already studied by him.

Tests were made in order to determine whether the presence of so small an amount of polysaccharide as 0.5% or less, which is the usual content of reducing substances in these TPT products, may be responsible for the precipitin reactions obtained. A polysaccharide, prepared as described in an earlier publication[17] from the culture filtrate of the H37 tubercle bacillus, was serially diluted in the same way as the protein antigens and added to all the antisera. No precipitation occurred with any of the antisera in any of the dilutions, as recorded in Table II.

When relatively small quantities of proteins are available, possibly more information concerning their chemical character and reactivity can be obtained by studying the titration capacities with acid and alkali than in almost any other way, except possibly by migration velocity determinations. Studies of the latter will be reported in the future. At present, however, only electrometric titration data will be considered. So far no significant differences had been detected between the five human strain proteins, even by means of the delicate immunological precipitin reaction. Nevertheless, it was obvious that the solubility of, for example, TPT-A10 was much less than that of any of the other proteins and, therefore, physico-chemical methods may be of value in finding differences indistinguishable in any other way.

Base Combining Capacity and Titration Curves of the Proteins.—Because of the small quantities of material available in the cases of certain fractions required for comparative analyses the following method of performing the titration was chosen. In all cases 250 mg. of the product was put into solution with the minimal amount of 0.1 *N* sodium hydroxide and the volume was made up to 25 cc. with freshly distilled water. The hydrogen ion activity of the solution was then determined by means of two hydrogen electrodes immersed in the solution, so that every reading could be checked. Hydrogen gas washed through water, potassium hydroxide and pyrogallic acid, was bubbled through the solution at a rapid rate, without discontinuing the flow of gas during the entire titration. The hydrogen electrodes, freshly platinized before each titration, were referred to a saturated calomel half cell through a saturated potassium chloride agar bridge. After the bridge was introduced into the system no difficulty with poisoning of the electrodes was experienced, and there was no difficulty in obtaining a potential which remained practically constant for an indefinite period of time. The two electrodes usually gave identical potentials. Otherwise the maximum variation between them was 0.0015 volt or a difference of 0.035 *p*H.

The foaming of the protein solutions was controlled by the addition of ether in the experiments recorded in this paper. In later experiments caprylic alcohol was used. The ether had the disadvantage of reducing the temperature to the neighborhood of 10°, but the temperature of the solution was recorded with each determination and the proper *p*H obtained with the use of Leeds and Northrup conversion tables. When the temperature was not 10° the *p*H was corrected to 10° by multiplying by a factor,

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(16) M. Heidelberger and F. E. Kendall, *J. Exptl. Med.*, **59**, 519 (1934).

(17) B. Munday and F. B. Seibert, *J. Biol. Chem.*, **100**, 277 (1933).

TABLE III

TITRATION OF H37-TPT

c, kg. per liter	Vol. cc.	Cc. 0.1 N NaOH added	Cc. 0.1 N HCl added	b	a	$\sqrt{\mu}$	Voltage (electrode #2)	pH, corrected to 10°	poh	h	oh	b' $\frac{b-a}{c}+\frac{h-oh}{c}$
0.00905	27.6	5.2	0	0.0188	0	0.137	0.9037	11.52	2.58	Negligible	0.002605	1.79
.00889	28.1		.5	.0185	.0018	.136	.8842	11.17	2.93	Negligible	.001170	1.76
.00877	28.5		.9	.0182	.0033	.135	.8631	10.79	3.31	Negligible	.000482	1.65
.00853	29.3		1.7	.0177	.0058	.133	.8205	10.03	4.07	Negligible	.000086	1.39
.00844	29.6		2.0	.0176	.0067	.133	.8071	9.79	4.31	Negligible	.000012	1.28
.00836	29.9		2.3	.0174	.0077	.132	.7731	9.19	4.91	Negligible	Negligible	1.17
.00799	31.3		2.7	.0166	.0084	.129	.6754	7.45	6.65	Negligible	Negligible	1.03
.00788	31.7		3.1	.0164	.0098	.128	.6392	6.80	7.30	Negligible	Negligible	0.85
.00778	32.1		3.5	.0162	.0109	.127	.6132	6.34	7.76	Negligible	Negligible	.69
.00764	32.7		4.1	.0159	.0125	.126	.5816	5.78	8.32	Negligible	Negligible	.45
.00759	32.9		4.3	.0158	.0131	.126	.5612	5.42	8.68	Negligible	Negligible	.36
.00752	33.1		4.5	.0157	.0136	.125	.5499	5.22	8.78	Negligible	Negligible	.28
.00748	33.4		4.8	.0155	.0143	.125	.5218	4.71	9.29	0.000019	Negligible	.16
.00744	33.6		5.0	.0154	.0149	.124	.5000	4.32	10.32	.000047	Negligible	.07
.00740	33.8		5.2	.0153	.0154	.124	.4568	3.55	10.45	.000278	Negligible	.02
.00729	34.3		5.7	.0151	.0166	.129	.4256	3.00	11.10	.001000	Negligible	−.07
.00718	34.8		6.2	.0149	.0178	.136	.4073	2.67	11.43	.002120	Negligible	−.10

(pKw at 10°)/(pKw at t°) = 14.375. This pKw value was obtained from data given by Michaelis.[18]

After the potential was determined aliquots of 0.1 N sodium hydroxide (0.1 to 0.5 cc.) were added, determining the potential after each addition, until a pH of 11 to 12 was reached, and then aliquots of 0.1 N hydrochloric acid were added in a similar way until a pH of 2 to 3 was reached.

Calculation of the Combining Capacities.—The system was checked before and after each titration by means of 0.1 N hydrochloric acid, made from constant boiling hydrochloric acid, and pH 1.087 was used as the standard value at 20°. Adequate corrections were made, in the same manner as by Simms,[19] for errors inherent in the entire system and for those due to variations in ionic strength of the solutions titrated, such as the activity coefficients. Accordingly, a blank titration with hydrochloric acid in water at 10° (obtained by the use of ether) was made and from the data a table was constructed of corrections to be applied to the hydrogen ion concentration at each $\sqrt{\mu}$ (μ = ionic strength = the concentration of hydrochloric acid). The limiting values of μ for base or acid in all of the experiments here reported were from 0.0001 to 0.025 M. Similarly a blank titration with sodium hydroxide in water was made at 10° (obtained by the use of ether) and a curve constructed from the data by plotting $\sqrt{\mu}$ (μ = ionic strength = the concentration of sodium hydroxide) against pH-log oh. In the equation pH-log $oh = pKw + \log f_{OH}$, f_{OH} is the activity coefficient of the hydroxyl ion. In this way, a table was constructed of the proper values for pH-log oh at every $\sqrt{\mu}$. From these pH-log oh values the pH determined for the solution under test was subtracted, giving the pOH. In the titrations of protein solutions as here recorded, μ was equal to b until a exceeded b and then it was equal to $b + (b-a)$.

The equivalents of base minus acid combined per kilogram of substance, were then calculated by means of the equation used by Simms,[19] $b' = (b-a)/c + (h-oh)/c$ in which b = concentration of strong base, a = concentration of strong acid, h = concentration of hydrogen ions, oh = concentration of hydroxyl ions, and c = concentration of protein. Since the molecular weight of none of the proteins studied was accurately known, all concentrations were expressed as kilograms of protein per liter. This would represent the molar concentration if the molecular weight were 1000.

The volume was changing throughout the titration, due to the repeated additions of alkali or acid, and, therefore, in the final calculation proper correction was made in a, b and c for each determination. A set of calculations, typical of those used for all of the curves in the paper, is given in Table III. In the curves, pH (activities) were plotted as abscissas against the corrected equivalents of base minus acid per kilo-

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(18) L. Michaelis, "Hydrogen Ion Concentration," Williams and Wilkins Co., Baltimore, Md., 1926, p. 26.

(19) H. S. Simms, *J. Gen. Physiol.*, **14**, 87 (1930).

gram of protein (b') found by the above equation.

Discussion of Results

Since all the proteins were insoluble in water and for solution required sufficient hydroxide to result in a high *p*H value, the curves plotted begin with the values obtained when the *p*H was most alkaline and extend to the most acid *p*H. In order that the corrections due to this procedure might not be too large, the *p*H was never carried beyond 11.5.

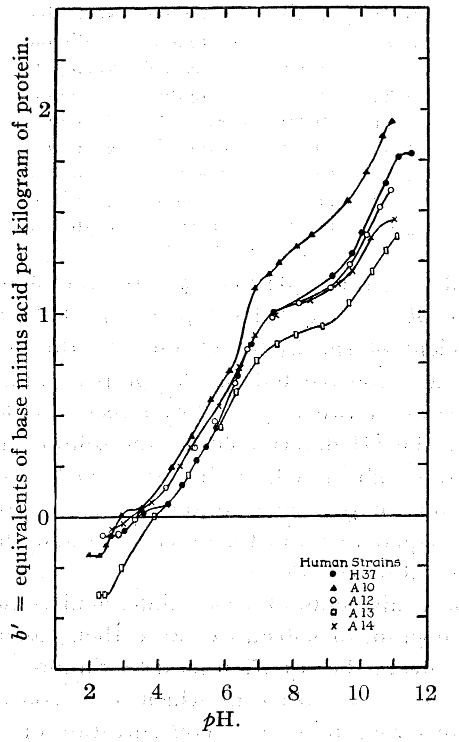

Fig. 1.

Figure 1 shows that the curves of the five human strain TPT's were similar. They were almost identical in the region between *p*H 2 and 6, and these similarities would exist regardless of what the real isoelectric points of the products might be. The curves of the TPT's from the bacillary strains H37, A12 and A14 are almost identical throughout; that of TPT-A13 shows a slightly less acidic substance, while that of TPT-A10 is more acidic. These similarities indicate a close correspondence in *p*K values for the different proteins and, therefore, presumably a similar amino acid structure. This probably explains why the precipitin tests showed identical crossing between all five proteins made from the human strain tubercle bacilli.

On the other hand, the curves of these human strains are quite different, in parts at least, from those of the TPT's made from acid-fast bacilli of other types (Fig. 2). The curves of the five human TPT proteins (represented by TPT-H-37 in Fig. 2) resemble that of the bovine TPT protein more than any of the others, especially in the portion of the curves more alkaline than *p*H 7.5, where the tyrosine, lysine and arginine groups are titrated. It is interesting to speculate on the bearing this may have on the fact that more immunological relationship was demonstrated, by means of the precipitin reaction, between these human TPT and the bovine TPT proteins than between the proteins of other type bacilli. It will be recalled that the bovine TPT antiserum crossed with the human TPT antigens almost as well as it did with itself, whereas the crossing, while real, was not as marked between the human TPT antisera and bovine TPT antigen. On the other hand, no crossing whatever occurred between the timothy and bovine TPT's. Furthermore, it has been shown by Henderson[20] that there is no immunological relationship between the *M. leprae* no. 1 TPT and the *M. leprae* no. 112 TPT, but that there is some crossing

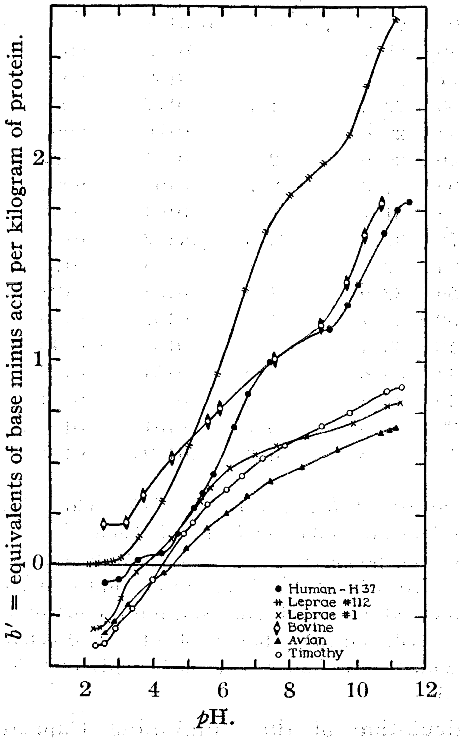

Fig. 2.

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[20] H. Henderson, in press.

between the Human-H37-TPT and the *M. leprae* no. 1 TPT and that the crossing between timothy and *M. leprae* no. 1 TPT's was very marked, facts which also correspond with the titration curves. These results indicate that further work along this line may be fruitful. Discussion as to the significance of different parts of the curves in relation to the nature of the products will be reserved for another paper.

I wish to express my appreciation to Dr. H. S. Simons for his advice in calculation of the base-binding capacities.

Summary

A comparative study of the proteins isolated from five different strains of human type tubercle bacillus culture filtrates, grown under identical conditions, yielded the following results:

The yields of protein were very much alike, *viz.*, about 0.2 g. per liter of original medium.

The nitrogen content of four of them was 14% and of the fifth 15.2%.

The tuberculin potency, determined by means of the skin test in tuberculous guinea pigs, showed some variation, but this was not marked. All five proteins were potent tuberculins.

All five proteins proved to be identical serologically, when compared by the precipitin reaction. They were type specific, in that they could be distinguished easily by this method from proteins made similarly from other acid-fast bacilli, as had been shown in earlier work. The protein from the bovine type tubercle bacillus, while distinctive, was related to some extent to the human type proteins. Polysaccharide was not responsible for the immunological reactions, since it gave no cross reactions with any of the antisera.

Acid–base-combining capacity curves throughout the range of *p*H 2 to 11, as determined by electrometric titration, using the hydrogen electrode, showed a much closer correspondence between the five proteins from human type tubercle bacilli than between them and proteins made similarly from other types of acid-fast bacilli.

PHILADELPHIA, PENNA. RECEIVED FEBRUARY 3, 1937

[CONTRIBUTION FROM INTERNATIONAL LEPROSY CENTER, RIO DE JANEIRO]

Hydnocarpic and Chaulmoogric Acids and Ethyl Esters

BY HOWARD IRVING COLE AND HUMBERTO CARDOSO

In making quantitative analyses of various chaulmoogra oils, it was necessary for us to know accurately the optical rotation and the boiling or melting points of pure hydnocarpic and chaulmoogric acids and their ethyl esters. The published data were not only incomplete but varied so widely that we found it necessary to prepare these substances in the pure state and redetermine their constants before proceeding with our analyses. Undoubtedly most of the errors found in the literature were due to impurities, since hydnocarpic acid is completely separated from chaulmoogric acid and from palmitic acid only with extreme difficulty. Hydnocarpic and chaulmoogric acids are optically active. They contain a double bond in the pentene ring and are classed theoretically as unsaturated acids as they absorb iodine or bromine in the theoretical amounts. On the other hand, being solid acids they behave physically more like the solid saturated acids, hence standard methods of separating unsaturated from saturated acids cannot be used for their isolation.

Methods of Separation

Pure chaulmoogric acid can best be obtained from the oil of *Oncoba echinata* or *Hydnocarpus alcalae* as these oils do not contain hydnocarpic acid. Analyses of chaulmoogra oils to date show no oil which contains hydnocarpic but not chaulmoogric acid, hence to obtain the former it must be separated from chaulmoogric acid. This was first accomplished qualitatively in 1905 by Power and his co-workers by fractional precipitation of their barium salts.[1] Other workers have used fractional crystallization of the free fatty acids or their salts, fractional distillation of the acids or methyl or ethyl esters, or some combination of these methods. Even so, complete purification is extremely difficult. For the preparation of pure hydnocarpic acid, *H. Wightiana* oil is recommended, as it does not contain palmitic acid whose physical properties are so close to those of hydnocarpic acid as to make complete separation of the latter next to impossible.

We have been able to separate completely hydnocarpic from chaulmoogric acids by employing a combination of

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[1] F. B. Power and M. Barrowcliff, *J. Chem. Soc.*, **87**, 888, 896 (1905).

fractional vacuum distillation of their ethyl esters in a Podbielniak high temperature fractionating apparatus[2] and fractional crystallization of the free fatty acids made from these esters. The free fatty acids of *Hydnocarpus Wightiana* oil were prepared by saponifying it and liberating the acids with sulfuric acid in the usual manner. They were washed free of mineral acid and glycerol with hot water, solidified and remelted to free them from water. The acids were esterified by dissolving them in five times their weight of 99% ethyl alcohol, then slowly mixing in one part by weight of concentrated sulfuric acid and allowing the mixture to stand overnight. An equal volume of water was then added and the ester extracted with ethyl ether, washed, and free acids removed by a 10% solution of sodium carbonate. The ethereal solution was washed several times with water, then dried with lumps of calcium chloride, filtered and the ether removed. The ethyl esters so prepared were distilled at 10-mm. pressure in a model B Podbielniak high temperature fractionating apparatus. One fractionation separated the ethyl hydnocarpate from the chaulmoograte though not from the other solid and liquid acids present. The fractions were saponified by adding twice their volume of 95% alcohol and 10% excess of potassium hydroxide dissolved in as little water as possible. Complete saponification results after five minutes of boiling. After dilution with 3 or 4 parts of hot water an excess of 15% sulfuric acid was added. The fatty acids rise and solidify on cooling. They were washed four times with hot water and then crystallized to constant melting point and optical rotation from 80% alcohol. Usually two crystallizations were sufficient. It was observed that the melting point was not an accurate criterion of the purity of the compound. The optical rotation, which is very high, was a more sensitive indication of purity as was also the appearance of the crystals. The crystals of pure hydnocarpic and of pure chaulmoogric acid both grow upward in branching forms from the melted acid, as it solidifies. Even a small amount of impurities inhibits this very characteristic growth, yielding instead a flat upper surface. As far as we know this peculiarity has not been reported before.

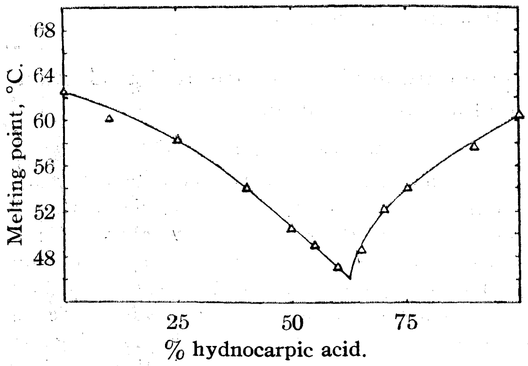

Fig. 1.—Melting point curve of palmitic and hydnocarpic acid mixtures.

The pure ethyl esters were prepared from these pure acids as outlined above and these were then redistilled in the Podbielniak apparatus. After taking the constants of these esters they were again changed to acids and crystallized two or more times. These acids showed no change in their constants from those first prepared. Ethyl esters from these acids when distilled gave the same boiling points, refractive indices and optical rotations as the preceding ones. Chaulmoogric acid and ethyl chaulmoograte prepared from *Oncoba echinata* oil gave the same constants as those from *H. Wightiana* oil. The constants of the pure acids and ethyl esters are given in Tables I and II.

TABLE I

CONSTANTS OF HYDNOCARPIC AND CHAULMOOGRIC ACIDS

Acid	Hydnocarpic	Chaulmoogric
Melting point, °C.	60.5	68.5
Specific rotation, $[\alpha]^{25}_D$	69.3	60.3
Iodine number (Hanus)	100.7	90.5
Neut. equivalent	251.8	280.9

Remarks: both the acids when pure grow upward in branching crystals from the melted acid as it solidifies.

TABLE II

CONSTANTS OF ETHYL HYDNOCARPATE AND CHAULMOOGRATE

Ester, ethyl		Hydnocarpate	Chaulmoograte
B. p. (10 mm.), °C.		184	206
Sp. rotation, $[\alpha]^{25}_D$		61.94	55.42
Specific gravity at	20/4	0.911	0.904
	25/4	.907	.901
	30/4	.904	.898
Refractive index at	20°	1.4597	1.4610
	25°	1.4578	1.4592
	30°	1.4558	1.4573

Melting Point Curves

It was noticed that even a small percentage of palmitic acid lowered the melting point of hydnocarpic acid to a surprising degree. The melting point curve of mixtures of these two acids was determined.

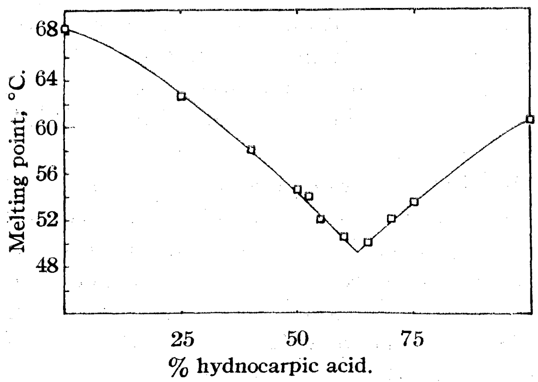

Fig. 2.—Melting point curve of chaulmoogric and hydnocarpic acid mixtures.

Power and Barrowcliff in their original work on hydnocarpic acid reported that systematic

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(2) W. J. Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 181 (1931); **5**, 119 (1933).

fractional crystallization of the free fatty acids of *H. Wightiana*, *H. anthelmintica* or *T. Kurzii* oils always yielded mixtures which melted at 48–50°C.[1] They concluded that they were dealing with a molecular mixture of chaulmoogric acid and its homolog, hydnocarpic acid. By making up mixtures of these two pure acids and plotting the melting point curve, it was found that the lowest melting mixture was not at the point of a molecular mixture. Mixtures of the two acids do show, however, a very sharp drop in melting point and a loss of the characteristic crystalline formation of the pure acids (Fig. 2).

Optical Rotation

Because of the very high specific optical rotations of hydnocarpic and chaulmoogric acids (69.3 and 60.3°, respectively), the determination of this value is a very convenient means of ascertaining the purity of the acid. Especially is this so when one is able to employ, as we have done, an electric sodium lamp in conjunction with a precision polarimeter. Two different observers have been able to check readings with each other within ±0.02°.

The specific optical rotation of chaulmoogric acid often has been reported too high because there has been mixed with it a small amount of the more optically active hydnocarpic acid. Thus Stanley and Adams[3] report +61.9°, Power and Barrowcliff[1], +62.1° and Hinegardner and Johnson,[4] +62.2°. Goulding and Akers[5] report +60.0° while we obtain +60.3°.

In the case of hydnocarpic acid most of the optical rotation values given in the literature are too low due to the presence of palmitic or even chaulmoogric acid. We, however, closely check the value given by Stanley and Adams,[6] +69.4°, although their value for ethyl hydnocarpate, +70.5°, evidently is in error.

CALCULATIONS FOR SPECIFIC OPTICAL ROTATION

Compound	Source, oil of	Grams	$CHCl_3$, cc.	Ang. rotn., 100-mm. tube	$[\alpha]^{25}_D$
Chaulmoogric acid	*H. Wightiana*	2.5526	25	+6.16°	+60.3°
Chaulmoogric acid	*O. echinata*	3.2175	25	+7.77°	+60.3°
Ethyl chaulmoograte	*O. echinata*	2.6479	25	+5.87°	+55.42°
Hydnocarpic acid	*H. Wightiana*	4.9422	50	+6.86°	+69.3°
Ethyl hydnocarpate	*H. Wightiana*	1.9978	25	+4.95°	+61.94°

Summary

The published data on the physical constants of hydnocarpic and chaulmoogric acids and ethyl esters are incomplete and inaccurate. Methods of preparation of the pure acids and ethyl esters are described and their physical constants have been determined. The melting point curves for mixtures of hydnocarpic and palmitic and of hydnocarpic and chaulmoogric acids have been determined.

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(3) W. M. Stanley and R. J. Adams, THIS JOURNAL, **48**, 2395 (1926).

(4) W. S. Hinegardner and T. B. Johnson, *ibid.*, **51**, 1503 (1929).

(5) E. Goulding and N. C. Akers, *Proc. Chem. Soc.* (London), **29**, 197 (1913).

(6) W. M. Stanley and Roger Adams, THIS JOURNAL, **51**, 1515 (1929).

RIO DE JANEIRO, BRAZIL RECEIVED FEBRUARY 9, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Some Reactions of Dihydroxyfluoboric Acid

BY J. W. KROEGER, F. J. SOWA AND J. A. NIEUWLAND[1]

A previous paper[2] from this Laboratory described the preparation and some of the properties of dihydroxyfluoboric acid and advanced a tentative structure for this compound. The present work was undertaken in order to throw some light on the structure of this acid and to present certain peculiar reactions which it undergoes.

The literature on the various acids of boron and fluorine has been reviewed by Meerwein and Pannwitz[3] and by the authors.[2] Meerwein describes a compound which he calls boron fluoride-dihydrate which is striking in its similarity to dihydroxyfluoboric acid. They have similar boiling and melting points, their indices of refraction and densities agree rather closely and the melting points of their dioxane derivatives are practically the same.

Dihydroxyfluoboric acid may be written in any of three ways

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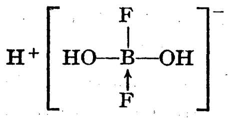
(1) The major portion of this work was completed before the death of Dr. Nieuwland in June, 1936.

(2) Sowa, Kroeger and Nieuwland, THIS JOURNAL, **57**, 454 (1935).

(3) Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).



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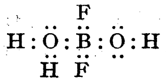

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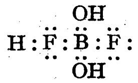

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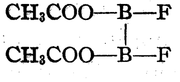
The first structure is the formal representation for this type of acid. The major part of the acid probably exists in the form of the second structure with the hydrogen ion coördinating with one of the hydroxyl groups. This is supported by the fact that dihydroxyfluoboric acid will combine with only one mole of boron trifluoride, probably through coördination with the second hydroxyl group. However, the possibility of the hydrogen ion coördinating with one of the fluorine atoms must also be admitted.

One hydrogen atom, as is represented in formula I, is available for salt formation. The others are alcoholic in their reactivity, or more properly, they resemble the hydrogen atoms in orthoboric acid. Sodium chloride reacts mole for mole with dihydroxyfluoboric acid with evolution of hydrogen chloride. The nickel salt crystallizes with three molecules of acid of crystallization as $Ni(H_2BO_2F_2)_2 \cdot 3H_3BO_2F_2$, but the unsolvated salt cannot be well characterized.

Dihydroxyfluoboric acid, in spite of the fact that it contains only two atoms of fluorine, forms boron trifluoride when it reacts. This is shown by the reaction with acetyl chloride and acetic anhydride, with oxygen compounds and with benzenediazonium chloride.

The hydrogen atoms of the two hydroxyl groups may be acetylated either with acetic anhydride or with acetyl chloride but, as yet, a stoichiometric equation cannot be written for the reaction. The products in the latter case are hydrogen chloride, acetic acid, acetic acid-boron fluoride [$(CH_3COOH)_2 \cdot BF_3$] and an acetoxy boron fluoride having the formula $(CH_3COOBF)_2$. This compound must be written in either of two ways



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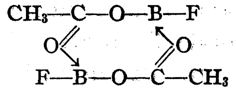

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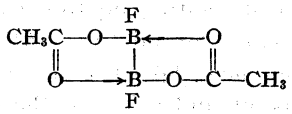
Acetoxyboron fluoride is a crystalline compound melting at 206–207° which sublimes with some decomposition *in vacuo*, is decomposed by water and most organic compounds containing oxygen (with the exception of acetyl chloride and acetic anhydride) and which has no reducing properties. Formula II is extremely unlikely since a seven electron shell about a boron atom is highly improbable. Formula I is more probable from a structural point of view. However, it is difficult to see how a boron-to-boron linkage could be formed from dihydroxyfluoboric acid. A third structure, a combination of the two previous, is somewhat more likely



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if the formation of a boron-to-boron link is admitted to be possible.

Experimental and Discussion

Preparation of Dihydroxyfluoboric Acid.—The preparation of this acid has been somewhat modified for the sake of speed and convenience.

Seven hundred and seventy grams of liquid hydrogen fluoride were run into a 1000-ml. copper beaker cooled in an ice-bath. After the hydrogen fluoride had cooled to approximately the temperature of the bath, 500 g. of boric oxide was added slowly. A rather violent reaction took place immediately and was accompanied by evolution of boron trifluoride. When about half the boric oxide had been added it was found necessary to run in 300 g. more hydrogen fluoride because of loss from evaporation. The reaction time for these amounts of reagents was two hours.

The copper beaker and contents were then heated to 80° for a half hour to drive off dissolved gases, after which the reaction mixture was poured into a Claisen flask. The liquid at this point weighed 1014 g. and since the theoretically possible quantity of acid is 903 g. it was concluded that the mixture still contained a large amount of dissolved gases. After two distillations in vacuum, 890 g. of pure dihydroxyfluoboric acid was obtained, b. p. 159–160° (745 mm.), 93–95° (25 mm.), 84–86° (16 mm.); m. p. 4.0–4.5°; n^{25}_{D} 1.3323; d^{25}_{4} 1.6560.

The molecular refraction of this acid could be calculated using the following linkage values: HO—B—OH[4] 7.05, H—F[5] 1.9 and B—F[6] 2.0. These values show the calculated molecular refraction of dihydroxyfluoboric acid to be 10.95. A carefully fractionated sample had the constants n^{30}_{D} 1.3414, d^{30}_{4} 1.6539. From these constants the observed molecular refraction is 10.68.

Conductivity of Dihydroxyfluoboric Acid.—The conductivity of the acid was determined with the usual Kohl-

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(4) Otto, unpublished work, University of Notre Dame. This value was calculated from the molecular refraction of orthoboric acid in dioxane (10.57).

(5) Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, 1931, p. 149.

(6) Klemm, *Z. anorg. allgem. Chem.*, **213**, 115 (1933). Klemm found the molecular refraction of boron trifluoride to be 6.0.

rausch assembly at 25°. The resistance was 2867 ohms, cell constant 56.052, specific conductivity 0.0195 mhos, molal conductivity 0.988 mhos.

Dioxane Derivative.—Five grams of dihydroxyfluoboric acid was treated with 5.9 g. of dioxane in 15 ml. of petroleum ether. The solid which separated was recrystallized from a mixture of dioxane and petroleum ether. The large, brittle, apparently non-hygroscopic crystals were powdered and found to melt at 139.5–140.5°. Calcd. for $C_4H_8O_2{\cdot}H_3BO_2F_2$ (%): boron, 6.28; fluorine, 22.1. Found: boron, 6.27; fluorine, 22.1.

Acetylation of Dihydroxyfluoboric Acid.—Approximately one-half mole (46.1 g.) of dihydroxyfluoboric acid was weighed into a flask cooled in an ice-bath. One and one-half moles of acetyl chloride (120 g.) was dropped in over a period of two hours. Hydrogen chloride came off immediately and was passed through a trap cooled in ice into a solution of sodium hydroxide. The evolution of hydrogen chloride practically ceased when about 85 ml. of acetyl chloride had been added; however, the remainder was run in in order to decrease the solubility of acetoxyboron fluoride in the reaction mixture. The flask was then warmed to about 40° and swept out with dry air to remove the remaining hydrogen chloride. It was found that the weight of the absorber had increased 42.8 g. Back-titration of the remaining sodium hydroxide indicated that 40.2 g. of hydrogen chloride had been absorbed. The discrepancy between this value, which is very near the calculated figure (40.1 g.), and the actual weight was probably due to some entrainment of acetyl chloride.

The reaction mixture was let stand overnight to permit crystallization of the acetoxyboron fluoride. The liquid was then decanted and the crystals were washed with a small amount of acetyl chloride. When crystallization did not take place the liquid reaction mixture was distilled directly and the residue was recrystallized from acetyl chloride from which it separated in long needles. The following are the results obtained from the experiment described above.

TABLE I

Product	B. p., °C.	Yield, g.	$n^{25}D$
HCl	.....	40.2	....
CH_3COOH	116–117	11.9	1.3730
$(CH_3COOH)_2{\cdot}BF_3$	64–66 (15 mm.)	51.5	1.3735
$(CH_3COOBF)_2$	M. p. 206–207°	19.3	....

Acetoxyboron fluoride was analyzed for boron and fluorine according to the procedure of Pflaum and Wenzke,[7] modified by decomposing the sample with sodium in liquid ammonia as described by Vaughn and Nieuwland.[8]

The acetyl determination was carried out in the following manner. Accurately weighed samples of acetoxyboron fluoride, usually about 1.5 g., were dissolved in 10 to 15 g. of absolute ethyl alcohol and refluxed for two hours. The mixture was then distilled until the temperature reached 85°, the distillate being collected in 250 ml. of 0.1 *N* sodium hydroxide. To the residue was added 15 g. of absolute alcohol and, after refluxing and distilling as before, the residue was again treated with absolute alcohol and the procedure repeated. All parts of the apparatus except the actual reaction flask were then rinsed with absolute alcohol which was added to the flask containing the distillate and 0.1 *N* sodium hydroxide. This was allowed to stand overnight and was then titrated with 0.1 *N* hydrochloric acid using phenolphthalein as an indicator. From this, the amount of ethyl acetate in the distillate could be found and consequently the percentage of acetyl in the original compound. It was found that the distillate contained only traces of boron and no fluorine. Two treatments with absolute alcohol, as described above, were sufficient to remove all the acetoxy but the third was always included to ensure certainty in the results. Eight to twelve hours was found to be ample for the saponification of the ethyl acetate. The results obtained were, calcd.: acetoxy, 66.46; boron, 12.16; fluorine, 21.39; total 100.0. Found: acetoxy, 65.4; boron, 12.16; fluorine, 21.09; total 98.7. A qualitative test for chlorine was found to be negative.

The molecular weight of acetoxyboron fluoride was determined ebullioscopically in acetyl chloride. Mathews and Fehlandt[9] give a value for the heat of vaporization of acetyl chloride at 50.4° equal to 87.14 ± 0.09 cal./g. The ebullioscopic constant calculated from this value was found to be 2.38 degrees per mole per kilogram. This constant was checked experimentally using pure naphthalene, which gave a value of 2.21. A series of ten determinations of the molecular weight of acetoxyboron fluoride gave an average value of 175.5 ± 3.1. This value is approximately twice the formula weight of 88.8 so the formula of the compound must be $(CH_3COOBF)_2$.

Although acetoxyboron fluoride is rather insoluble in acetyl chloride, this solvent appears to be the only one in which there is no possibility of decomposition. It was thought that some light might be thrown upon the structure of this compound by a determination of the molecular refraction. The constants given below were all determined at 25°. Those for the pure solvent, acetyl chloride, were: d_4 1.0958, nD 1.38613, *MR*D calcd. 16.314, *MR*D obs. 16.827. The values for the solution were d_4 1.1009, nD 1.38646, c_2 0.0072116 moles/mole. These data give a value for the molecular refraction of 29.029. The calculated value, omitting the third valency of the boron atoms, is 30.268. This omission causes the calculated value to be low by at least one or two units; however, considering the extreme dilution of the solution and the lack of knowledge concerning the disposition of the third boron linkages, these values are in surprisingly good agreement.

Acetoxyboron fluoride is insoluble in most organic solvents and is decomposed by water and those containing oxygen. It may be crystallized from trimethyl borate if done quickly but on standing in contact with the solvent for more than a day it is decomposed.

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(7) Pflaum and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **4**, 392 (1932).

(8) Vaughn and Nieuwland, *ibid.*, **3**, 274 (1931).

(9) Mathews and Fehlandt, THIS JOURNAL, **53**, 3212 (1931).

Referring to Table I it may be seen that, on the basis of one mole of dihydroxyfluoboric acid reacting, there are found in the products 0.984 atom of boron, 2.08 atoms of fluorine, 1.93 atoms of non-carbonyl oxygen but 3.594 atoms of hydrogen. The empirical formula for dihydroxyfluoboric acid is $H_3BO_2F_2$ and since the above value for hydrogen is definitely beyond the experimental error of the determination it is difficult to explain this discrepancy. Actual determinations of hydrogen by combustion methods gave a value of 3.37% as compared to the calculated value of 3.61%. In addition, when dihydroxyfluoboric acid is treated with sodium chloride exactly one mole of hydrogen chloride is given off.

One-third mole of dihydroxyfluoboric acid (28 g.) was dissolved in 200 g. of redistilled ether-boron fluoride b. p. 121–122° and 40 g. (excess) of powdered C. P. sodium chloride was added. The mixture was refluxed for three days and the hydrogen chloride which came off was dissolved in sodium hydroxide solution. Back-titration showed that 11.1 g. of hydrogen chloride had been absorbed. The calculated value, assuming only one hydrogen in dihydroxyfluoboric acid to be replaced, is 12.2 g. The reaction was very slow and probably did not go to completion.

Nickel Salts.—Since the nickel salt of dihydroxyfluoboric acid is quite readily prepared it was decided to utilize this as an additional method for characterizing the acid. This salt may be prepared without difficulty by dissolving nickelous carbonate or chloride in the acid but the oxides and hydroxide apparently do not react.

Slightly less than the calculated quantity of nickelous carbonate was dissolved in dihydroxyfluoboric acid by warming. The product, which solidified on cooling, was recrystallized from a small amount of pure acid. The resulting dark-green crystals were filtered with suction in a closed Gooch crucible and were quickly pressed dry on filter paper, then were analyzed for nickel using dimethylglyoxime. Calcd. for $Ni(H_2BO_2F_2)_2 \cdot 3H_3BO_2F_2$: Ni, 12.3. Found: Ni, 11.9, 12.1. This salt melted at 120°.

The salt was heated carefully and intermittently at 155–160° and 12 mm. pressure for a total period of twelve hours. Samples were removed at intervals of two to three hours and analyzed and in this way a material was obtained which corresponded to nickel dihydroxyfluoborate. Calcd. for $Ni(H_2BO_2F_2)_2$: Ni, 26.1. Found: Ni, 26.2, 26.2. This material, light green in color, is readily converted by heating for two to three hours at 200° and 12 mm. pressure to a creamy, fluffy powder. Calcd. for $Ni(HBO_2F)_2$, 31.8% Ni and for $Ni(BF_2O)_2$, 31.1% Ni; found, 31.0% Ni. The first salt might be formed by loss of hydrogen fluoride from the original material and the second by loss of water. The latter possibility was found to be the case since a small amount of water actually was collected during the second period of heating, that at 200°.

The cream colored salt was ignited in air at 900° for ten hours. The resulting greenish-black powder contained 60.1% Ni. After an additional ten hours of heating the percentage of nickel had risen to 61.7%. This material contained boron but no fluorine and was apparently a mixture of nickelous oxide and metaborate. Beginning with the original dark green crystalline salt, the solubility in water of the various compounds became smaller as heating progressed. The cream colored salt was only slightly soluble in water but soluble in dilute acids. The final oxide–metaborate mixture was insoluble in water and acids and in order to analyze for nickel the samples had first to be fused with sodium pyrosulfate. The remaining compounds were quite soluble in water.

Formation of Orthoboric Acid.—Dihydroxyfluoboric acid is decomposed by low-molecular weight acids, alcohols, esters, ketones, aldehydes and ethers, with the exception of dioxane, to form orthoboric acid and boron fluoride. This decomposition is apparently regulated by the ease of formation of the boron fluoride complex of the second reactant. Thus trichloroacetic acid, the boron fluoride complex of which is stable only at low temperatures, will not react with dihydroxyfluoboric acid even when melted, whereas acetic acid, which forms a stable addition compound boiling at 141–142°, reacts almost immediately.

The reaction always involves one mole of dihydroxyfluoboric acid and two moles of the second reactant. While the actual decomposition may be represented by the following scheme

$$3H_3BO_2F_2 \longrightarrow 2BF_3 + H_3BO_3 + 3H_2O$$

where the boron fluoride then forms a complex with the second reactant, it is difficult to understand why the additional amount of the oxygen compound is necessary. That is, three moles of the acid actually require six moles of the second reactant.[10] Two moles of an ether are required to combine with the boron fluoride liberated and either two or four moles of an acid or an alcohol ($ROH \cdot BF_3$ and $RCOOH \cdot BF_3$ or the more stable $(ROH)_2 \cdot BF_3$ and $(RCOOH)_2 \cdot BF_3$). In either case the amount is less than the six moles actually required. The boron fluoride and the orthoboric acid cannot be estimated accurately since the water formed in the reaction causes a secondary decomposition.

The boric acid from these decompositions, when filtered and pressed dry on filter paper,

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(10) This was determined by preparing tubes containing identical amounts of dihydroxyfluoboric acid and varying amounts of the reactant, centrifuging and weighing the orthoboric acid formed. The boron fluoride was also estimated where the second reactant formed a complex, stable to distillation, as in the case of ether, acetic acid and methyl and ethyl acetates.

contained from 6 to 10% fluorine, and 16.7 to 17.0% boron (calcd. for H_3BO_3, 17.5% B). The melting point was always about 148–149° and since pure boric acid melts at 175–176° it was thought that there must be some other compound present. When thoroughly washed with the secondary reactant the material contained no fluorine, the melting point rose to 175–176° and the percentage of boron rose to the calculated value, 17.5%. The same thing could be accomplished by drying in a vacuum over potassium hydroxide for two weeks. After drying for twelve hours at 110° the material contained no fluorine and was found to be metaboric acid, m. p. 175–176°, 24.6% B, calcd., 24.6%.[11]

Samples of pure orthoboric acid were moistened with ether–boron fluoride, acetic acid–boron fluoride and methyl acetate–boron fluoride and after filtering and pressing dry on filter paper, were found to have melting points between 149 and 151° and contained considerable amounts of fluorine. Apparently this was the explanation for the low melting points.

Orthoboric acid is also formed by the action of water on dihydroxyfluoboric acid, m. p. 175°, calcd. % B 17.5; found, 17.4.

Preparation of Fluorobenzene.[12]—The best results were obtained using a ratio of two moles of dihydroxyfluoboric acid to one of the diazonium salt. One-quarter mole of benzenediazonium chloride was prepared to which was added one-half mole (42 g.) of dihydroxyfluoboric acid while cooling to below 10°. The mixture was stirred for forty-five minutes, then filtered and the light-green precipitate was washed with small amounts of alcohol and ether: yield of salt, 43 g.; decomposition point, 84°. This salt was decomposed by warming and formed 11.8 g. of fluorobenzene, b. p. 84–85°. If this salt were $C_6H_5N_2BF_2(OH)_2$ the yield of fluorobenzene was 25%, whereas if the compound were $C_6H_5N_2BF_4$ the yield was 50%.

The purest salt was obtained by using a ratio of one mole of dihydroxyfluoboric acid to one of the diazonium compound. The yield was extremely poor but the salt decomposed at 85°. One-half gram of this material, accurately weighed, was decomposed by heating and the evolved gas was analyzed. The volumes were corrected for pressure, temperature and the vapor tension of water. A total of 115 ml. of gas was collected over mercury. After washing with water 56 ml. of nitrogen remained. Calculated: total, 116.8 ml.; BF_3, 58.4 ml.; N_2, 58.4 ml. These results indicate that the salt was benzenediazonium fluoborate $C_6H_5N_2BF_4$ and that it was about 95% pure.

Acknowledgment.—The authors are indebted to Dr. R. R. Vogt for valuable advice and criticism and to Dr. M. M. Otto, Messrs. V. P. Osweiler, C. R. Montgomery and F. J. Froning for assistance in various parts of this work.

Summary

1. Dihydroxyfluoboric acid has been shown to contain one strongly acidic and two non-acidic hydrogen atoms.

2. Several reactions of dihydroxyfluoboric acid have been discussed and their products identified.

3. Acetoxyboron fluoride has been prepared by acetylation of dihydroxyfluoboric acid and a proposed structure has been advanced.

NOTRE DAME, INDIANA RECEIVED MARCH 3, 1937

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[11] It was thought that the presence of another compound might appear in a determination of molecular weight. Trimethyl borate was chosen as a solvent. The melting point was found to be −29.4 ± 0.1° and the cryoscopic constant, determined experimentally using naphthalene, was 4.68 ± 0.1° per mole per kilogram. However, it was found that the boric acids dissociated in this solvent. Thus, metaboric acid had an apparent molecular weight of 29.5.

[12] "Organic Syntheses," **13**, 46 (1933).

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Steady-State Rate of a Chain Reaction for the Case of Chain Destruction at Walls of Varying Efficiencies[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

Bursian and Sorokin's[4] treatment of the rate of a chain reaction with destruction of the chain carriers at the wall considers only the case that every chain carrier striking the surface is destroyed. It is, however, well known that walls possess different efficiencies, as is shown, for example, by experiments with hydrogen atoms. The efficiencies may range from the order of 100% to <0.001%. Recently, Kassel and Storch[5] have treated the problem for a spherical vessel with varying efficiencies of the chain-breaking process. For the average concentration of chain carriers $\bar{n}$, transcendental equations are obtained. The reaction rate is equal to $Kc\bar{n}$, where c is the concentration of the gas with which the chain carrier undergoes reaction and K is the velocity coefficient.

In the present paper, the consequences of the theory for the experimental study of an unknown reaction are discussed. In particular, the influence of vessel diameter on the rate is described quantitatively by tabulation, since this can be done without knowledge of the reaction mechanism and since it serves adequately to explore regions of special kinetic interest. It is also shown that the exact transcendental equations can be replaced with good approximation by simple equations of the type customarily employed in kinetic work. This will serve to show the extent to which former treatments are valid.

It has often been assumed[6,7] that, in a quiescent mixture where chain carriers reach the wall by diffusion only, the concentration of chain carriers may be determined from the equation

$$\bar{n} = n_0 \Big/ \left(\frac{\text{const.}}{pd^2} - \alpha\right) \qquad (1)$$

in which n_0 is the rate of chain initiation per unit volume, $\alpha\bar{n}$ is the net rate of chain branching (α being the difference between the velocity coefficients of the rate of chain branching and the rate of chain destruction in the volume if such exists), p is the pressure, and d is a linear dimension of the reaction vessel. The term $(const./pd^2)\bar{n}$ would then be the rate of chain destruction at the wall, the constant being in some way dependent on the efficiency of chain destruction. The limitations of equation 1 do not seem always to have been fully appreciated. As will be seen later, the equation is approximately correct only for chain initiation in the gas phase, for relatively high efficiencies of chain destruction, and for vessel diameters and pressures that are not small compared with those necessary to induce explosion under the same conditions.

The two cases of chain initiation at the wall and in the gas phase will now be considered. For both cases chains are assumed to branch in the gas phase and to break principally at the wall.

Chain Initiation at the Wall

The concentration of chain carriers, n, at any distance, a, from the center of the spherical vessel of radius, r, is found by integrating the differential equation expressing that the change of concentration with time due to diffusion and net rate of branching is zero and introducing the boundary condition that the net rate of branching throughout the volume is equal to the rate of surface destruction of chains minus the rate of production of new chains at the surface. The rate of destruction of chains at the surface is ϵ times the rate at which the chain carriers strike it, ϵ being the efficiency of chain destruction with values ranging from 0 to 1.

The introduction of the boundary condition to determine the integration constant A in the expression n = f (a) (equation 4 of Kassel and Storch[5]) requires the determination of the total number of chain carriers in the volume, that is, solution of $\int_0^r 4\pi a^2 n da$. Substituting for A

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[4] Bursian and Sorokin, *Z. physik. Chem.*, **B12**, 247 (1931).

[5] Kassel and Storch, THIS JOURNAL, **57**, 672 (1935).

[6] N. Semenoff, "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935, pp. 49–51, 56–57.

[7] C. N. Hinshelwood and A. T. Williamson, "The Reaction Between Hydrogen and Oxygen," Oxford University Press, 1934, pp. 48–49.

equation 15[8] of Kassel and Storch, and solving for the average concentration of chain carriers, one obtains

$$\bar{n} = \frac{\gamma m_0}{\left[\frac{\epsilon r}{\lambda}\frac{1 - \sqrt{\alpha/\mathrm{D}}\,\lambda\,\mathit{ctn}\,\sqrt{\alpha/D}\,r}{1 - \sqrt{\alpha/D}\,r\,\mathit{ctn}\,\sqrt{\alpha/D}\,r} - 1\right]\alpha} = \frac{\gamma m_0}{\left[\frac{\epsilon r}{\lambda}\frac{1-\lambda/r}{1 - \sqrt{\alpha/D}\,r\,\mathit{ctn}\,\sqrt{\alpha/D}\,r} + \epsilon - 1\right]\alpha} \qquad (2)$$

m_0 is the rate of chain initiation per unit area and γ is the ratio of surface to volume and is equal to $3/r$. Therefore, γm_0 is the volume equivalent of the rate of chain initiation. D is the diffusion coefficient and λ is the mean free path.

$\bar{n}$ can have only positive values. The condition $\bar{n} = \infty$ marks the limit of the steady state where the reaction becomes explosive. Beyond this limit, that is, within the explosive region, equation 2 would give negative values for $\bar{n}$. It follows by inspection of equation 2 that for $\bar{n}$ to be positive $\sqrt{\alpha/D}\,r$ must not exceed π and as $\sqrt{\alpha/D}\,r$ approaches π, ϵ must approach 1.

Important deductions regarding the influence of experimental conditions on $\bar{n}$ may be made from the power series expansion of equation 2 for the limiting condition that $\sqrt{\alpha/D}\,r$ is close to zero. The term $1 - \sqrt{\alpha/D}\,r\,\mathit{ctn}\,\sqrt{\alpha/D}\,r$ reduces to $\frac{1}{3}\frac{\alpha r^2}{D}$. If $D = \frac{\bar{v}\lambda}{4}$[9] ($\bar{v}$ being the average molecular velocity) and $\lambda/r \ll 1$, equation 2 becomes

$$\bar{n} = \frac{\gamma m_0}{\left(\frac{\epsilon r}{\lambda}\frac{3D}{\alpha r^2} + \epsilon - 1\right)\alpha} = \frac{\gamma m_0}{{}^3/_4\frac{\epsilon\bar{v}}{r} - (1 - \epsilon)\,\alpha} \qquad (3)$$

For small values of ϵ the positive term in the denominator becomes identical with the coefficient of the rate of chain destruction. In contradistinction to the corresponding term in equation 1, it is inversely proportional to the radius and independent of pressure if ϵ is independent of pressure. The functional dependence of ϵ is determined by the mechanism of the chain-destroying reaction in which will enter the natures of the surface and the chain carrier and possibly pressure, temperature and mixture composition. If ${}^3/_4\frac{\epsilon\bar{v}}{r}\left(= \frac{\epsilon\bar{v}}{4}\gamma\right) \gg (1 - \epsilon)\,\alpha$, $\bar{n}$ becomes independent of vessel size and dependent on pressure, temperature and mixture composition only to the extent that $m_0/\epsilon\bar{v}$ is dependent on these factors. Experimentally, this region is of particular interest, since it allows a direct kinetic investigation of the ratio of the chain-initiating reaction to the efficiency of chain destruction. This much-needed separation of variables finds its counterpart in the independent kinetic investigation of α from the determination of the explosion regions in a diagram of any two of the variables pressure, temperature, mixture composition, vessel size.

The condition ${}^3/_4\frac{\epsilon\bar{v}}{r} \gg (1 - \epsilon)\,\alpha$ can be approached by making r small or by decreasing α in a manner that does not simultaneously decrease ϵ to the same or to a greater degree. This would demand that the functional dependence of ϵ on any variable shall be a milder one than the dependence of α on that variable. As far as pressure and mixture composition are concerned this limitation would seem to be the usual case. α may be made small by reducing the pressure of the reactants involved in the branching reaction. Frequently, α can be made small by decreasing the temperature but here one often encounters very complex functional dependencies of both α and ϵ. This is illustrated by the reaction between oxygen and higher hydrocarbons.[10]

Whenever the rate of a chain reaction is found to be independent of diameter there exist only two alternatives. Either the above-discussed case applies or chains are both initiated and destroyed in the gas phase. In the latter case, however, the rate will remain independent of diameter for all diameters, whereas in case chains are initiated and destroyed at the wall, branching causes the rate eventually to increase with increasing diameter. No such well-defined criterion for distinguishing these two cases is obtained by varying the pressure, temperature or mixture composition.

It has usually been found difficult to determine with accuracy the dependence of the reaction rate on diameter. There may be various reasons for this, the most obvious being the difficulty of controlling, experimentally, properties of the surface on which m_0 and ϵ depend. Often, it has only been possible to state that a reaction rate is either independent of or roughly dependent on some power of the diameter. In the light of the

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[8] More exactly, the term $\frac{\epsilon\bar{v}r}{4}\sin\sqrt{\alpha/D}\,r$ in their equation 15 should be replaced by $\frac{\epsilon\bar{v}r}{4}\sin\sqrt{\alpha/D}\,(r - \lambda)$.

[9] The difference between this value of D and the usual value $\bar{v}\lambda/3$ arises from the assumption that all free paths are equal as has been done in Kassel and Storch's[5] treatment.

[10] Von Elbe and Lewis, THIS JOURNAL, **59**, 976 (1937).

TABLE I

$\frac{1}{\pi}\sqrt{\alpha/D}\,r_0$	0		0.318		0.605		0.701		0.800		0.933		1	
$\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$	0		.358		1.65		2.60		4.46		14.80		∞	
ϵ_7/ϵ_4	$6/\pi^2$		.630		0.700		0.739		0.798		0.913		1	
r/r_0	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_8}{\bar{n}_5}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_8}{\bar{n}_5}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_8}{\bar{n}_5}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_8}{\bar{n}_5}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_8}{\bar{n}_5}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_8}{\bar{n}_5}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_8}{\bar{n}_5}$
0	1	1	0.93	0.96	0.73	0.87	0.62	0.82	0.47	0.76	0.19	0.67	$3.3\,\lambda/r_0$	0.61
0.1	1.11	1	1.04	.96	.79	.87	.66	.82	.49	.76	.19	.67	$3.3\,\lambda/r_0$	.61
.2	1.25	1	1.15	.96	.86	.87	.72	.82	.53	.76	.20	.67	$3.4\,\lambda/r_0$	.62
.3	1.43	1	1.31	.96	.96	.87	.78	.82	.58	.76	.22	.67	$3.5\,\lambda/r_0$	.63
.4	1.67	1	1.55	.96	1.09	.87	.89	.82	.64	.76	.24	.68	$3.7\,\lambda/r_0$	.65
.6	2.50	1	2.23	.95	1.54	.86	1.23	.83	.85	.77	.29	.71	$4.5\,\lambda/r_0$	.70
.8	5.0	1	4.43	.94	2.91	.85	2.25	.84	1.50	.80	.48	.79	$7.0\,\lambda/r_0$	.80
1.0	∞	1	∞	.94	∞	.85	∞	.84	∞	.85	∞	.92	∞	1

above results and others to be presented later, even such comparatively rough experimental data may provide considerable knowledge concerning the reaction mechanism.

The dependence of the reaction rate on diameter will now be investigated quantitatively. For given values of ϵ, λ, D and α there exists a vessel radius r_0 at which the rate becomes explosive, that is, $\bar{n} = \infty$. For radii $r < r_0$ the slow steady-state rate will be established, that is, $\bar{n}$ is finite and positive.

From equation 2 and $\lambda/r \ll 1$

$$\frac{\epsilon r}{\lambda} = (1 - \sqrt{\alpha/D}\,r_0\,ctn\,\sqrt{\alpha/D}\,r_0)\frac{r}{r_0}(1 - \epsilon) \qquad (4)$$

ϵ is small compared with 1 unless $\sqrt{\alpha/D}\,r_0$ is very close to π. If, for example, λ/r is of the order 10^{-3} corresponding to low pressures (a few mm. mercury) and ordinary vessel dimensions, ϵ is greater than the order of 0.1 only when $\sqrt{\alpha/D}\,r_0$ exceeds 0.99 π. For higher pressures, $\sqrt{\alpha/D}\,r_0$ must approach even closer to π before ϵ reaches this value.

Combining equations 2 and 4, the exact equation becomes

$$\frac{\alpha\bar{n}}{\gamma m_0} = \frac{1}{(1 - \epsilon)\left(\frac{1 - \sqrt{\alpha/D}\,r_0\,ctn\,\sqrt{\alpha/D}\,r_0}{1 - \sqrt{\alpha/D}\,r\,ctn\,\sqrt{\alpha/D}\,r}\frac{r}{r_0} - 1\right)} \qquad (5)$$

If $\bar{n}$ is independent of diameter the function $\alpha\bar{n}r_0/\gamma m_0 r$ must be constant. Values of this function calculated from equation 5 for $\sqrt{\alpha/D}\,r_0$ from 0 to π and r/r_0 from 0 to 1 are given in Table I. The corresponding values of $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$ are given in the second horizontal line. It is seen that the range of diameters within which the reaction rate is reasonably independent of diameter widens for increasing values of $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$. Thus, for $\epsilon r_0/\lambda = 0$, about a 10% increase in the value of the function occurs between $r/r_0 = 0$ and 0.1, whereas for $\epsilon r_0/\lambda = r_0/\lambda$ the same increase occurs between $r/r_0 = 0$ and 0.4. It is plain that for otherwise identical conditions the replacement of a vessel with a wall of high chain-breaking efficiency by one with low chain-breaking efficiency should markedly increase the dependence of the reaction rate on vessel diameter.

The following considerations give some idea of the magnitude of ϵ for a given value of $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$.

In the usual experiments the pressure may be between a few millimeters and 1 atmosphere, for which λ is of the order 10^{-2} to 10^{-4} cm., respectively. Values of the explosion radius r_0 depend on a number of conditions. In actual experiments it will probably not be less than the order of 10 cm. Thus, when $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon} =$ 14.80, ϵ would not be larger than 0.01 to 0.0001, depending on the above pressure range. This example illustrates that the effect of ϵ on the dependence of the rate on diameter becomes noticeable only in vessels with walls having extremely small chain-breaking efficiencies.

The influence of ϵ on the reaction rate itself is very pronounced over the whole range of values from 0 to 1, the rates decreasing with increasing ϵ.

Previously, non-transcendental equations were obtained for $\bar{n}$ on the basis of Bursian and Sorokin's treatment, which strictly apply only to the case of large efficiency of chain destruction (ϵ close to 1) and to the neighborhood of the explosion limit.[6] It will now be shown that for this condition, namely, $\sqrt{\alpha/D}\,r$ close to π, equation 2 can be reduced to a non-transcendental equation that describes with good approximation all the essential features of the theory. The term $1 - \sqrt{\alpha/D}\, r \, ctn \sqrt{\alpha/D}\, r$ now reduces, in the limit, to $1 \Big/ \left(\frac{\pi}{r}\sqrt{\alpha/D} - 1\right)$ or the general form $2^x/(y^{2^x} - 1)$ where $x = 0, 1, 2, 3 \ldots$ and $y = (\pi/r)\text{-}\sqrt{\alpha/D}$. The desired reduction is obtained for $x = 1$. If $\lambda/r \ll 1$ equation 2 becomes

$$\bar{n} = \frac{\gamma m_0}{\left[\frac{\epsilon r}{2\lambda}\left(\frac{\pi^2 D}{\alpha r^2} - 1\right) + \epsilon - 1\right]\alpha} \qquad (6)$$

To compare equation 6 with equation 2 for the influence of diameter, $\epsilon r/\lambda$ must be expressed as a function of r_0. This expression is obtained readily from equation 4, since $\sqrt{\alpha/D}\, r_0$ is also close to π. Thus

$$\frac{\epsilon r}{\lambda} = \frac{2}{\frac{\pi^2 D}{\alpha r_0^2} - 1}\,\frac{r}{r_0}\,(1 - \epsilon) \qquad (7)$$

Combining equations 6 and 7

$$\frac{\alpha\bar{n}}{\gamma m_0} = \frac{1}{(1 - \epsilon)\left(\frac{\frac{\pi^2 D}{\alpha r^2} - 1}{\frac{\pi^2 D}{\alpha r_0^2} - 1}\,\frac{r}{r_0} - 1\right)} \qquad (8)$$

A direct comparison of equations 8 and 5 is furnished by the tabulation of the ratio $\bar{n}_8/\bar{n}_5$ for the entire range of $\sqrt{\alpha/D}\, r_0$ and r/r_0. This is given in Table I. It is seen that equation 8 follows the trend of equation 5 over practically the entire range. Even in the columns toward the right of Table I it represents the region in which the rate is independent of vessel size over much the same range of r/r_0 as equation 5. The gradual improvement of the numerical agreement toward the left of Table I is accompanied by an increasing but always unimportant discrepancy in $\frac{\epsilon r}{\lambda}\frac{1}{1 - \epsilon}$ introduced through equation 7. Thus by the approximate treatment reaction vessels possess apparent chain-breaking efficiencies that are smaller than the actual ones. Ratios of such apparent to actual efficiencies calculated from equations 7 and 4 are listed in the third horizontal line in Table I.

The comparison of equations 2 and 6 will now be made in a perfectly general way, to include variations not only in diameter but in any physical condition such as pressure, temperature and mixture composition. According to equation 2, the condition for explosion may be written

$$1 - (\sqrt{\alpha/D}\, r)_0 \, ctn \, (\sqrt{\alpha/D}\, r)_0 = \left(\frac{\epsilon r}{\lambda}\frac{1}{1 - \epsilon}\right)_0 \qquad (9)$$

and according to equation 6

$$\frac{2}{\left(\frac{\pi^2 D}{\alpha r^2}\right)_0 - 1} = \left(\frac{\epsilon r}{\lambda}\frac{1}{1 - \epsilon}\right)_0 \qquad (10)$$

If $(\sqrt{\alpha/D}\, r)_0$ is close to 0, the left-hand sides of equations 9 and 10 become $\frac{1}{3}\left(\frac{\alpha r^2}{D}\right)_0$ and $\frac{2}{\pi^2}\left(\frac{\alpha r^2}{D}\right)_0$, respectively. Since $\sqrt{\alpha/D}\, r$ is ordinarily also close to 0, both equations 2 and 6 after substituting equations 9 and 10, respectively, become identical, namely

$$\frac{\alpha\bar{n}}{\gamma m_0} = \frac{1}{1 - \epsilon\left(\frac{(\alpha r^2/D)_0}{\alpha r^2/D} - 1\right)} \qquad (11)$$

It is now clear why $\bar{n}_8/\bar{n}_5$ should have been found equal to 1 for $\frac{\epsilon r}{\lambda}\frac{1}{1 - \epsilon}$ equal to 0 (Table I).

Let us now consider $\sqrt{\alpha/D}\, r \ll (\sqrt{\alpha/D}\, r)_0$ for any value of the latter between 0 and π. The more complete expansion of $1 - \sqrt{\alpha/D}\, r \, ctn \sqrt{\alpha/D}\, r$ is given by $\frac{1}{3}\frac{\alpha r^2}{D} + \frac{1}{45}\frac{\alpha^2 r^4}{D^2} + \ldots$, whence $\frac{1}{1 - \sqrt{\alpha/D}\, r \, ctn \sqrt{\alpha/D}\, r} = \frac{3D}{\alpha r^2}\frac{1}{1 + \frac{1}{15}\frac{\alpha r^2}{D} + \ldots}$. The corresponding term in equation 6, $\frac{1}{2}\left(\frac{\pi^2 D}{\alpha r^2} - 1\right) = \frac{\pi^2 D}{2\alpha r^2}\left(1 - \frac{1}{\pi^2}\frac{\alpha r^2}{D}\right)$ becomes, for small values of $\sqrt{\alpha/D}\, r$, equal to $\frac{\pi^2}{2}\frac{D}{\alpha r^2}\frac{1}{1 + \frac{1}{\pi^2}\frac{\alpha r^2}{D}}$. As $\sqrt{\alpha/D}\, r$ becomes small the two denominators, namely, $1 + \frac{1}{15}\frac{\alpha r^2}{D}$ and $1 + \frac{1}{\pi^2}\frac{\alpha r^2}{D}$ approach 1 almost simultaneously. Thus, both equations 2 and 6 approach an identical form almost simultaneously (apart from an unimportant numerical factor). This explains why the range over which the rate may be considered independent of diameter should have been found almost equally well described by equation 8 (Table I).

It has now been demonstrated that the approximate treatment (equation 6) is satisfactory for small chain-breaking efficiencies from slow reaction to explosion and for any chain-breaking efficiency in the region where the reaction rate is reasonably independent of diameter. The equation applies strictly to the range for which it was derived, namely, large chain-breaking efficiencies and reaction rates close to explosion. There remains the intermediate range in which discrepancies between approximate and exact treatments would be greatest. This range cannot be investigated in a general way because the functional dependencies of ϵ, α, D and λ vary for different reactions. Only for changes in vessel size is a comparison possible. Judging from the rather satisfactory agreement (Table I) it may be expected that for most kinetic purposes with emphasis placed on trend rather on exact numerical agreement, the approximate treatment will be found satisfactory.

Chain Initiation in the Gas Phase

In this case the concentration of chain carriers at any distance from the center of the spherical vessel is found by integrating the differential equation expressing the fact that the change of concentration with time due to diffusion, net rate of branching and initiation is zero and introducing the boundary condition that the net rate of branching plus the rate of chain initiation throughout the volume is ϵ times the rate at which chain carriers strike the surface. Using the same treatment as before, except that now $n = f(a)$ and the integration constant A are given by equations 13 and 14,[11] respectively, of Kassel and Storch,[5] one obtains

$$\bar{n} = \frac{n_0}{\alpha}\,\frac{\frac{3D}{\alpha r^2}(1 - \lambda/r)}{\frac{1 - \lambda/r}{1 - \sqrt{\alpha/D}\,r\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r} - \frac{\lambda}{\epsilon r}(1 - \epsilon)} - 1 \quad (12)$$

where n_0 is the rate of chain initiation per unit volume.

As before, in order that $\bar{n}$ be positive $\sqrt{\alpha/D}\,r$ must not exceed π and as $\sqrt{\alpha/D}\,r$ approaches π, ϵ approaches 1.

For $\sqrt{\alpha/D}\,r$ close to 0, the series expansion

$$\frac{{}^1/_3\,\frac{\alpha r^2}{D}}{1 - \sqrt{\alpha/D}\,r\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r} = \frac{1}{1 + \frac{1}{15}\frac{\alpha r^2}{D} + \ldots}$$

becomes equal to $1 - \frac{1}{15}\frac{\alpha r^2}{D}$ and equation 12 reduces to, for $\lambda/r \ll 1$

$$\bar{n} = \frac{n_0}{\frac{15D}{r^2}\,\frac{1}{1 + \frac{5\lambda}{\epsilon r}(1 - \epsilon)} - \alpha} \quad (13)$$

It is seen that if $\frac{5\lambda}{\epsilon r}(1 - \epsilon) \ll 1$ the rate of chain destruction is inversely proportional both to the pressure and to the square of the diameter. If, in addition, $15D/r^2 \gg \alpha$, the reaction rate is proportional to the square of the diameter. If $\frac{5\lambda}{\epsilon r}(1 - \epsilon) \gg 1$, equation 13 becomes

$$\bar{n} = \frac{n_0}{{}^3/_4\,\frac{\epsilon \bar{v}}{r} - \alpha} \quad (14)$$

and the rate of chain destruction is now inversely as the diameter. In this case, if $3/4\ \epsilon\bar{v}/r \gg \alpha$ the reaction rate is proportional to the first power of the diameter.

It immediately becomes apparent that for the case of chain initiation in the volume, the region in which the reaction rate is proportional to the first or second power of the diameter acquires similar importance for the study of reaction kinetics as the region of independence of diameter in the case of wall initiation. In the region of strict diameter-squared proportionality, $\bar{n}$ is proportional to n_0/D, whereas in the region of diameter to the first-power proportionality it is proportional to $n_0/\epsilon\bar{v}$. The separate investigation of α can be made by a study of the explosion regions as mentioned before.

Equation 12 will now be investigated for the dependence of reaction rate on diameter. $\epsilon r/\lambda$ is again given by equation 4. Combining equations 4 and 12, one obtains

$$\frac{\alpha\bar{n}}{n_0} = \frac{1}{{}^1/_3\,\frac{\alpha r^2}{D}\left(\frac{1}{1 - \sqrt{\alpha/D}\,r\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r} - \frac{r_0/r}{1 - \sqrt{\alpha/D}\,r_0\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r_0}\right)} - 1 \quad (15)$$

Table II contains values of the functions $\frac{\alpha\bar{n}}{n_0}\frac{r_0}{r}$ and $\frac{\alpha\bar{n}}{n_0}\frac{r^2_0}{r^2}$ calculated from equation 15 for $\sqrt{\alpha/D}\,r_0$ from 0 to π and r/r_0 from 0 to 1. Wherever these functions can be considered constant with respect to r/r_0, the rate is proportional to the first or second power, respectively, of the diameter. It is seen that the range of diameters within which the reaction rate is reasonably proportional to the first power of the diameter decreases as $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$ increases and that even in the most favorable case ($\epsilon r_0/\lambda = 0$) it does not begin until small fractions of the explosion diameter. For $\epsilon r_0/\lambda = r_0/\lambda$ there is no range over which the diameter to the first-power proportionality holds. In the latter case there is a large range of diameters over which the reaction rate is proportional to the square of the diameter. This range is considerably decreased and is shifted toward larger ratios of r/r_0 as $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$ decreases. It is seen that most of this narrowing and shifting of the range occurs for large values of $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$. There is very little additional change below 14.80.

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[11] Strictly, a factor of $1 - \lambda/r_0$ should be inserted in the numerator of equation 14 of Kassel and Storch.

TABLE II

$\frac{1}{\pi}\sqrt{\alpha/D}\,r_0$	0			0.605			0.933			0.987			0.999			1.000		
$\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$	0			1.65			14.80			75.43			1000			∞		
r/r_0	$\frac{\alpha\bar{n}}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar{n}}{n_0}\frac{r^2_0}{r^2}$	$\frac{\bar{n}_{16}}{n_{12}}$	$\frac{\alpha\bar{n}}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar{n}}{n_0}\frac{r^2_0}{r^2}$	$\frac{\bar{n}_{16}}{n_{12}}$	$\frac{\alpha\bar{n}}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar{n}}{n_0}\frac{r^2_0}{r^2}$	$\frac{\bar{n}_{16}}{n_{12}}$	$\frac{\alpha\bar{n}}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar{n}}{n_0}\frac{r^2_0}{r^2}$	$\frac{\bar{n}_{16}}{n_{12}}$	$\frac{\alpha\bar{n}}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar{n}}{n_0}\frac{r^2_0}{r^2}$	$\frac{\bar{n}_{16}}{n_{12}}$	$\frac{\alpha\bar{n}}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar{n}}{n_0}\frac{r^2_0}{r^2}$	$\frac{\bar{n}_{16}}{n_{12}}$
0	1	∞	0.61	0.73	∞	0.53	0.19	∞	0.41	0.04	∞	0.37	0.003	∞	0.37	0	0.66	0.37/.92
0.02	1.02	51	.61	.74	37	.53	.20	10	.42	.06	2.8	.49	.02	.82	.81	.01	.66	.92
.04	1.04	26	.61	.76	19	.53	.22	6	.45	.07	1.7	.57	.03	.74	.86	.03	.66	.92
.07	1.07	15	.61	.79	11	.53	.24	3.4	.49	.09	1.25	.65	.05	.71	.90	.05	.66	.92
.1	1.11	11	.61	.82	8.2	.53	.26	2.6	.52	.11	1.07	.71	.07	.69	.91	.07	.66	.93
.2	1.25	6.3	.61	.92	4.6	.54	.33	1.6	.60	.18	.89	.79	.14	.70	.91	.14	.68	.93
.3	1.43	4.8	.61	1.05	3.5	.55	.41	1.4	.66	.26	.86	.83	.22	.72	.92	.22	.72	.93
.4	1.67	4.2	.61	1.23	3.1	.56	.53	1.3	.68	.36	.89	.85	.32	.79	.92	.31	.78	.93
.6	2.50	4.2	.61	1.87	3.1	.57	.87	1.5	.75	.66	1.10	.89	.61	1.0	.94	.60	1.0	.95
.8	5.0	6.3	.61	3.7	4.7	.59	1.87	2.3	.79	1.5	1.9	.92	1.4	1.8	.96	1.4	1.7	.97
1.0	∞	∞	.61	∞	∞	.60	∞	∞	.84	∞	∞	.96	∞	∞	1.0	∞	∞	1.0

The influence of ϵ on the reaction rate itself varies with $\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$ and r/r_0. It is largest for small values of these functions and becomes rather negligible for large values.

Again, the essential features of the theory can be expressed with good approximation by a non-transcendental equation derived from equation 12 for the condition that $\sqrt{\alpha/D}\,r$ is close to π. Using the series expansion given earlier in connection with equation 6, equation 12 for $\lambda/r \ll 1$ reduces to

$$\bar{n} = \frac{(6/\pi^2)\,n_0}{\left[\frac{\pi^2 D}{\alpha r^2} - 1 - \frac{2\lambda}{\epsilon r}(1-\epsilon)\right]\alpha} - 1$$

Since $\frac{\pi^2 D}{\alpha r^2} - 1$ and $\frac{2\lambda}{\epsilon r}(1-\epsilon)$ become vanishingly small for $\sqrt{\alpha/D}\,r$ close to π, the reduction may be carried further to

$$\bar{n} = \frac{(6/\pi^2)\,n_0}{\frac{\pi^2 D}{r^2}\,\frac{1}{1+\frac{2\lambda}{\epsilon r}(1-\epsilon)} - \alpha} \qquad (16)$$

It can again be demonstrated that equation 16 is for most kinetic purposes a satisfactory substitute for equation 12, as was shown earlier for equation 6. This will be perhaps sufficiently evident from the similarity of equations 13 and 16, which were derived for opposite extremes. It is demonstrated in Table II specifically for the case of diameter dependence by the columns ($\bar{n}_{16}/\bar{n}_{12}$).

Summary

The steady-state treatment of chain reactions in which chains are broken at walls of varying efficiencies is discussed. Two cases are considered, namely, chain initiation at the wall and in the gas phase. It is shown that under conditions of negligible branching there exist characteristic relations between rate and vessel diameter. This may be used for a kinetic study of the unbranched reaction, whereas the branching reaction may be studied from explosion limits. The influence of vessel diameter on the rate has been described quantitatively for varying chain-breaking efficiencies. It is also shown that the exact transcendental equations may be replaced with good approximation by simple non-transcendental equations.

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The Combustion of Paraffin Hydrocarbons[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

Norrish[4] has proposed a chain mechanism of the oxidation of hydrocarbons which describes the slow and explosive reaction of methane in agreement with a number of observations; it does not describe the phenomenon of the low-temperature explosion peninsula and other associated effects ("cool" flames, maximum in the reaction rate found in the neighborhood of 350° for all paraffin hydrocarbons above methane); it also does not explain the formation of methyl alcohol in large quantities in the oxidation of rich mixtures of propane[5] at low temperatures, a fact which, according to Pease, can best be explained by a chain mechanism involving monovalent (alkyl and alkoxyl) radicals. Pease's mechanism applies exclusively to this observation and does not describe the experimental facts accounted for by Norrish's scheme. A more extensive mechanism was proposed by Ubbelohde[6] but was not treated kinetically.

In the present paper a mechanism of the oxidation of paraffin hydrocarbons is proposed which is believed to allow a more comprehensive interpretation of chemical and kinetic facts.

Chemistry of the Oxidation

It is generally recognized that the oxidation of hydrocarbons passes through the aldehyde stage to the ultimate products carbon monoxide, carbon dioxide and water. Since aldehyde added in small amounts to a hydrocarbon-oxygen mixture very markedly decreases the induction period,[7] the latter is interpreted as the period during which the aldehyde gradually accumulates.[4,8] Its presence appears to be necessary for the creation of chain centers responsible for the subsequent chain reactions in the gas phase. Thus, the chemistry of hydrocarbon and aldehyde oxidation being intimately related, it is advantageous to consider first the aldehyde oxidation.

Oxidation of Aldehydes.—Two oxidation reactions of aldehydes have been reported.

One is a catalytic surface reaction[9] which is particularly pronounced at low temperatures (not much above room temperature) but decreases toward higher temperatures. This reaction passes through a peracid stage to carbon dioxide as the chief oxide of carbon, the process being strongly accelerated by coating the surface with potassium chloride.[9b]

The other reaction is a gas-phase reaction unquestionably of the chain type;[9,10] it proceeds through a step-wise degradation to lower aldehydes[10a] by the intermediate formation of peracids,[9,10d] carbon monoxide being the only oxide of carbon formed. Formaldehyde cannot degrade further but is oxidized to carbon monoxide and water. The chain character of the gas-phase reaction is demonstrated by the inhibitory action of packing the vessel and by the large quantum yield in the photochemical oxidation of acetaldehyde.[11]

The primary products in the photochemical reaction consist largely of monovalent radicals arising from the photodissociation[12]

$$CH_3CHO + h\nu = CH_3 + HCO \qquad (1)$$

In the absence of oxygen this would be followed by[12a]

$$CH_3 + CH_3CHO = CH_4 + CH_3CO \qquad (2)$$

In the presence of oxygen it is plausible that O_2 adds directly to the CH_3CO forming a peroxidic radical. This radical is assumed to react further with acetaldehyde in a manner analogous to reaction (2). Since the only radicals regenerated

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(1) Published by permission of the Director, U. S. Bureau of Mines, and Director, Coal Research Laboratory, Carnegie Institute of Technology. (Not subject to copyright.) Read at the meeting of the American Chemical Society, Pittsburgh, Pa., Sept., 1936.

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(4) Norrish, *Proc. Roy. Soc.* (London), **A150**, 36 (1935).

(5) (a) Pease, THIS JOURNAL, **57**, 2296 (1935); (b) also, Pease and Munro, *ibid.*, **56**, 2034 (1934).

(6) Ubbelohde, *Proc. Roy. Soc.* (London), **A152**, 354 (1935).

(7) (a) Bone and Hill, *ibid.*, **A129**, 434 (1930); (b) Bone and Allum, *ibid.*, **A134**, 578 (1931); (c) Steacie and Plewes, *ibid.*, **A146**, 583 (1934).

(8) Bone and Gardner, *ibid.*, **A154**, 297 (1936).

(9) (a) Hatcher, Steacie and Howland, *Can. J. Research*, **7**, 149 (1932); (b) Pease, THIS JOURNAL, **55**, 2753 (1933).

(10) (a) Pope, Dykstra and Edgar, *ibid.*, **51**, 1875 (1929); (b) Fort and Hinshelwood, *Proc. Roy. Soc.* (London), **A129**, 284 (1930); (c) Askey, THIS JOURNAL, **52**, 974 (1930); (d) Bodenstein, *Z. physik. Chem.*, **B12**, 151 (1931).

(11) Bowen and Tietz, *J. Chem. Soc.*, 234 (1930); *cf.* Carruthers and Norrish, *ibid.*, 1036 (1936).

(12) (a) Leermakers, THIS JOURNAL, **56**, 1537 (1934); (b) Blacet, and Roof, *ibid.*, **58**, 278 (1936); (c) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

are CH_3CO and $CH_3CO(OO)$ the chain would then be carried on essentially by the reactions

$$\mathrm{CH_3CO(OO) + CH_3CHO = CH_3CO + CH_3CO(OOH)} \qquad (3)$$

$$\mathrm{CH_3CO + O_2 = CH_3CO(OO)} \qquad (4)$$

At low temperatures the reaction stops at the peracid stage, the latter compound being formed in large amounts. If it is now assumed that chains are broken in the gas phase by

$$\mathrm{2CH_3CO(OO) = CH_3COOOOCCH_3 + O_2} \qquad (5)$$

a kinetic consideration shows that the reaction rate should be proportional to the square root of the light intensity and to the first power of the aldehyde concentration but independent of the oxygen concentration, as is found experimentally.[11]

At higher temperatures the reaction does not stop at the peracid stage and is assumed to lead to degradation reactions in rapid succession. This may be represented by

$$\begin{array}{r}\mathrm{RCH_2CO \xrightarrow{O_2} CO + H_2O + RCO \xrightarrow{O_2} \ldots\ CO + H_2O + CH_3CO} \\ \big\downarrow \mathrm{O_2} \quad (6) \\ \mathrm{HCHO^* + CO + OH}\end{array}$$

It is not entirely justified to exclude the formation of intermediate aldehydes as has been done here. However, intermediate aldehyde stages seem to be traversed rapidly to formaldehyde. The approximate formulation (6) possesses kinetic advantages. The formation of formaldehyde in the last step of reaction (6) is accompanied by the evolution of approximately 110 kcal. which is adequate to excite the observed luminescence ("cool" flames).[6]

Comparison of the chain length in thermal decomposition and oxidation of aldehydes shows that the latter is far more rapid than the former.[10a,11,13]

Chain Mechanism in Hydrocarbon Oxidation.—Once aldehyde has been formed by some mechanism which will be discussed later, it partly oxidizes catalytically to peracid, the latter being destroyed to form carbon dioxide or, as may be supposed, sometimes dissociating into two monovalent radicals, a fraction of which enters the gas phase to give rise to chains. The carbon dioxide-forming reaction being catalyzed by potassium chloride, the production of chain carriers and therefore the rate of hydrocarbon oxidation should be slowed down in a potassium chloride-coated vessel as is found experimentally.[14]

The mechanism for the oxidation of methane exclusive of branching reactions may be visualized as follows:

Chain initiation

$$\mathrm{HCHO + O_2 \xrightarrow{Surface} HCO(OOH) \xrightarrow{Surface} HCOO + OH} \qquad \mathrm{I}$$

Methane oxidation chain

$$\mathrm{OH + CH_4 = CH_3 + H_2O} \qquad \mathrm{II}$$

$$\mathrm{CH_3 + O_2 = HCHO + OH} \qquad \mathrm{III}$$

Aldehyde oxidation chain

$$\mathrm{OH + HCHO = HCO + H_2O} \qquad \mathrm{IV}$$

$$\mathrm{HCO + O_2 = HO_2 + CO} \qquad \mathrm{V}$$

$$\mathrm{HO_2 + HCHO = CO + H_2O + OH} \qquad \mathrm{VI}$$

Chain breaking

$$\mathrm{OH \xrightarrow{Surface} destruction} \qquad \mathrm{VII}$$

Direct association of oxygen in reaction V in binary collisions would seem to be very improbable. Reaction VI conforms to the fact that the ultimate products of the chain oxidation of formaldehyde in the gas phase are carbon monoxide and water.[10b]

While most of the formaldehyde is oxidized in the gas phase, some of it diffuses to the wall and reacts there to form more radicals according to (I). Many of these radicals remain adsorbed on the wall and eventually recombine to form saturated products. Some diffuse into the gas phase and generate new reaction chains. Thus, the process accelerates slowly from an unnoticeable to a measurable reaction during which the formaldehyde increases to a concentration easily detectable analytically.[15] In agreement with this are the experiments of Bone and Gardner,[8] who found a pronounced auto-accelerating curve for the increase of formaldehyde concentration with time.[16]

For the oxidation of higher hydrocarbons the mechanism is analogous. The radical CH_3 now becomes RCH_2, etc. Such large radicals presumably can add O_2 directly in a binary collision forming RCH_2OO, thus allowing an explanation of the formation of methyl alcohol in mixtures

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(13) Sickman and Allen, THIS JOURNAL, **56**, 1251 (1934). See also Fletcher, *Proc. Roy. Soc.* (London), **A146**, 357 (1934).

(14) (a) Pease and Chesebro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928); (b) Pease, THIS JOURNAL, **51**, 1839 (1929); (c) Taylor and Riblett, *J. Phys. Chem.*, **35**, 2667 (1931).

(15) Bone and Wheeler, *J. Chem. Soc.*, **81**, 535 (1902), and many other investigators since.

(16) The exponential character of the curve does not seem to justify the opinion of these authors "that the formation of formaldehyde probably did not begin until after half way through the induction period."

containing a large excess of hydrocarbon. On analogy with Pease's[5a] mechanism we may write

$$RCH_2CH_2 + O_2 = RCH_2CH_2OO \longrightarrow RCHO + CH_3O \quad (7)$$

$$CH_3O + RCH_2CH_3 = CH_3OH + RCH_2CH_2 \quad (8)$$

The decomposition of the alkyl peroxide radical is in agreement with the similar behavior of saturated alkyl peroxides.[17] Now, the experimental data show that less alcohol is formed as the oxygen content of the mixture is increased[5a] and that finally the alcohol yield becomes negligible. Thus, in mixtures of 1 part of octane with 11 to 13 parts of oxygen, no alcohols are found.[10a] This fact may be accounted for by the destruction of methoxyl according to

$$CH_3O + O_2 = CO + H_2O + OH \quad (9)$$

It is evident that in very rich mixtures methyl alcohol and aldehydes should appear in approximately equal amounts, a fact borne out by experiment.[5a]

A further refinement of the proposed mechanism and enhancement of its chemical plausibility is obtained from experiments on the slow oxidation of rich mixtures of methane and ethane at high pressures.[18] In the case of methane, methyl alcohol is formed, the yield increasing with decrease in the oxygen content. It is only in mixtures containing a few per cent. of oxygen that the yield becomes large. The other products are carbon monoxide, carbon dioxide and water and a small amount of formaldehyde. In the case of ethane, both ethyl and methyl alcohols appear besides carbon monoxide, carbon dioxide and water. There are appreciable amounts of acetaldehyde, acetic acid and also methane. Increasing the oxygen content causes a decrease in the yields of the oxygenated organic compounds, but it is noted that the ethyl alcohol yield decreases very much more than the methyl alcohol.[18d]

To harmonize these facts, the following reaction will be assumed

$$CH_3 + O_2 + CH_4 = CH_3OOH + CH_3 \quad (10)$$

This reaction is favored by high pressures and rich mixtures. Concerning a direct proof of methyl peroxide formation, it is noted that this substance, as indeed others representative of this group, is highly unstable[17] and that there is no hope of isolating it from the reacting mixture, as has indeed been the experience.[7a,b,15,18b,c,d]

Methyl peroxide possesses a strong tendency to condense with aldehydes. With formaldehyde, oxydimethyl peroxide, $CH_3OOCH_2(OH)$, is formed.[17] The latter compound seems to possess a particular ability to dissociate at the peroxidic bond. This is evident by comparison of its behavior with that of the related compound dioxydimethyl peroxide, $CH_2(OH)O-OCH_2(OH)$, in alkaline solution. The latter decomposes into molecular hydrogen and formic acid* and the former partly into atomic hydrogen[17] and formic acid, indicating that the oxydimethyl peroxide undergoes primary dissociation into the radicals CH_3O and $CH_2(OH)O$.

It may be assumed, therefore, that in the high-pressure oxidation of methane, methyl peroxide and formaldehyde condense to oxydimethyl peroxide, which decomposes into radicals. A methyl alcohol chain then becomes possible involving reactions 8 (the hydrocarbon being methane), 10 and the last discussed condensation–dissociation reaction. The products carbon monoxide and formaldehyde would arise from reactions 9 and III. The mechanism thus accounts for the decreasing yield of methyl alcohol with increasing oxygen content. For the formation of carbon dioxide it is possible to propose other reactions such as the heterogeneous decomposition of oxydimethyl peroxide.[17]

If the same scheme is applied to the high-pressure oxidation of ethane, that is, starting correspondingly with ethyl peroxide and acetaldehyde, it is evident that methyl alcohol should appear as an oxidation product instead of water. The experimental facts concerning the total yields of oxygenated compounds and the ratio of the methyl and ethyl alcohol yields are also readily accounted for. Acetic acid probably arises from another decomposition reaction of oxydiethyl peroxide yielding also ethyl alcohol. Methane may arise from a side reaction conceivably involving the destruction of acetaldehyde.

It may be assumed that alkyl peroxide radicals condense similarly with aldehydes and dissociate at the peroxidic bond as postulated above. This would constitute a branching reaction (to be called peroxide branching) since two new free

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[17] Rieche, "Alkylperoxide und Ozonide," Steinkopff, Dresden, 1931.

[18] (a) Yoshikawa, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **10**, 305 (1931); see *Abs. Sci. Papers Inst. Phys. Chem. Res.*, **15**, 1931; (b) Newitt and Haffner, *Proc. Roy. Soc.* (London), **A134**, 591 (1931); (c) Newitt and Bloch, *ibid.*, **A140**, 426 (1933); (d) Newitt and Szego, *ibid.*, **A147**, 555 (1934).

* See Rieche and Meister's [*Ber.*, **68B**, 1465 (1935)] mechanism of the decomposition of oxymethyl peroxide.

valences are thus created. Evidently the probability of this reaction would depend on the lifetime of the R-OO radical (reaction 7) and thus is favored by lower temperatures. This would explain the pronounced reactivity[14a,19] and explosivity[20] particularly of normal paraffins in the neighborhood of 350°, and the accompanying phenomenon of "cool" flames[10a,14a,20,21] (see Fig. 1). If the hydrocarbon contains side groups then, as first pointed out by Pope, Dykstra and Edgar,[22] the degradation reaction 6 on reaching the tertiary carbon atom would leave a ketone instead of an aldehyde. The ketone cannot be expected to undergo condensation with peroxide and thus the fact can be explained that isoparaffins exhibit the low temperature phenomena to a lesser and lesser degree as the structure of the molecule is more condensed.[20b,22]

The radicals arising from the peroxide branching reaction are expected to oxidize further. Judging from the reaction energy involved in the oxidation, other bonds may be broken and assuming OH to be the favored radical, as many as five OH may result.

If one assumes with Norrish that the explosion at higher temperatures is predominantly of the branched chain type, another branching reaction with a positive temperature coefficient must be advanced. Expressions suitable for the description of explosion limits and other facts are obtained by assuming that branching occurs in ternary collisions of the radical HO_2 with aldehyde and oxygen. The reaction may be supposed to involve the primary oxidation of the aldehyde to peracid and subsequent dissociation of the latter. From an energy point of view the reaction is plausible. It will be referred to as the peracid branching reaction. Altogether three free valences appear, yielding on further oxidation three OH. The reaction may be written

Peracid branching

$$HO_2 + O_2 + HCHO \text{ or } RCHO \longrightarrow 3OH \qquad \text{VIII}$$

In order to account for the influence of mixture composition on the ignition temperature, a reaction competing with reaction V will be assumed, namely

Formaldehyde condensation

$$HCO + HCHO \longrightarrow (CH(OH)CHO) \xrightarrow{O_2} 2CO + H_2O + OH \qquad \text{IX}$$

That such an assumption is not improbable, particularly if one of the reactants is a radical, is shown by the fact that condensation products of formaldehyde, polyoxymethylenes, are known, which at 240° in the gas phase retain molecular weights amounting to 6 to 8 fold HCHO.[23]

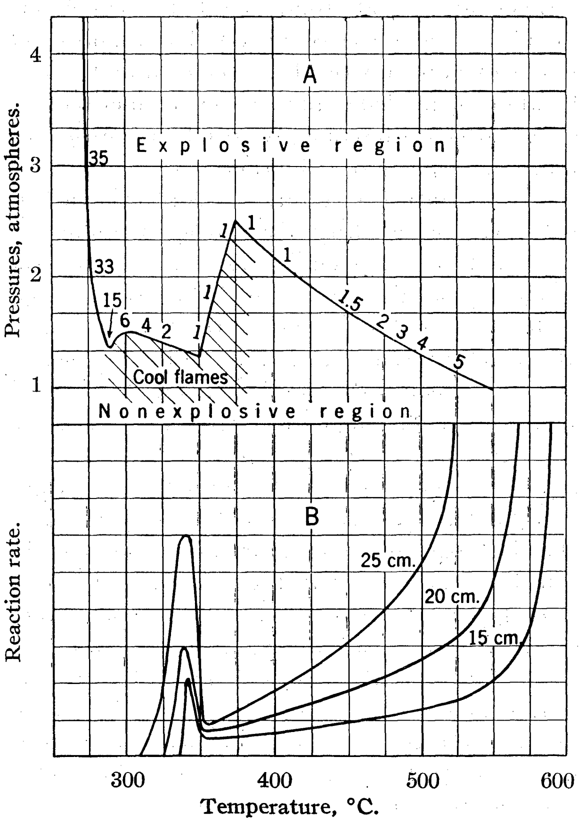

Fig. 1.—*Curve A:* Ignition region of 3.1% hexane in air mixture. Region of "cool flames" marked by shaded area. Induction periods in seconds indicated by numbers along curve (Townend, Cohen and Mandlekar reference 20b). *Curve B:* Reaction rates of 11.1% pentane in oxygen mixture at different pressures (Neumann and Aivazov reference 19a).

No crucial experiments seem to be available to rule out the possibility that methane explosions are thermal in nature in which case the peracid branching reaction VII could be dispensed with. However, the branched chain theory is adequate to describe the experimental results cited below.

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[19] (a) Neumann and Aivazov, *Nature*, **135**, 655 (1935); (b) Beatty and Edgar, THIS JOURNAL, **56**, 102 (1934).

[20] (a) Townend and Mandlekar, *Proc. Roy. Soc.* (London), **A141**, 484 (1933); *ibid.*, **A143**, 168 (1933); (b) Townend, Cohen and Mandlekar, *ibid.*, **A146**, 113 (1934); (c) Townend ,and Chamberlain, *ibid.*, **A154**, 95 (1936); (d) see also Prettre, Dumanois and Lafitte, *Compt. rend.*, **191**, 329 (1930).

[21] Emeléus, *J. Chem. Soc.*, 1733 (1929); Prettre, *Bull. soc. chim.*, **51**, 1132 (1932); Beatty and Edgar, THIS JOURNAL, **56**, 112 (1934).

[22] Pope, Dykstra and Edgar, *ibid.*, **51**, 2203 (1929).

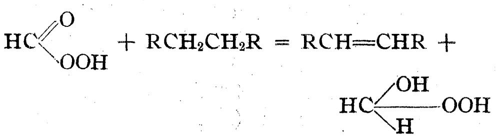
[23] Beilstein "Handbuch der organischen Chemie," 4th edition, Vol. I, 1918, p. 568.

Primary Reactions.—For the kinetic treatment, the only specific assumption concerning the primary reaction between hydrocarbon and oxygen that need be made is that it is, as mentioned above, an aldehyde producing reaction. It is difficult to obtain experimental facts pertaining to this reaction because it is obscured by the ensuing chain reaction. However, it appears to the authors that the most probable assumption is a catalytic reaction. If, for example, a mixture of methane and oxygen is passed through a porous porcelain filter at atmospheric pressure and 440°, formaldehyde and some methyl alcohol are found.[24] The presence of the latter substance is explained readily on the basis of catalytic combination of methane and oxygen to methyl peroxide, which subsequently reacts as explained under high pressure oxidation.

A possibility for a direct gas-phase reaction with oxygen, at least for higher paraffins, is suggested by Stephens'[25a] experiments on the oxidation of alkyl-substituted benzenes. That higher paraffin hydrocarbons react with oxygen at temperatures as low as 130° to form explosive peroxides among other products, is well known.[25b]

At very high temperatures one may also consider the primary reaction to involve atoms or radicals originating from thermal dissociation.

Secondary Reactions.—Before leaving the chemical part of this paper, attention may be called to the fact that there are a number of secondary reactions of the non-chain type. Some of those which lead to oxygen-ring compounds have been studied by Ubbelohde.[26] A particularly common type is one that gives rise to the simultaneous appearance of olefins and oxyalkyl peroxides.[5b] This reaction can best be understood as the interaction of a newly formed peracid molecule with a hydrocarbon molecule.


(11)

$$\mathrm{HC(=O)OOH + RCH_2CH_2R = RCH{=}CHR + HC(OH)(H)OOH} \quad (11)$$

Mono-oxyalkyl peroxides are surprisingly non-explosive,[17] which accounts for the fact that they can be isolated at the high temperatures of the oxidation. They have been observed in the oxidation of hydrocarbons from ethane[7a] upward only, which is understandable in view of the fact that peracid cannot react with methane, as in reaction 11. By condensation with aldehydes they give rise to more complicated products.[27]

Kinetics of the Oxidation

Methane.—In the following, the symbols k_1, k_2, etc., are the velocity coefficients for the corresponding reactions in the mechanism I to IX. Concentrations in the gas phase are indicated by brackets. By assuming weak adsorption the rate of reaction I becomes on the basis of the Langmuir isotherm

$$(k_1/d)\,[\mathrm{HCHO}][\mathrm{O_2}] \qquad (12)$$

where d is diameter of the vessel.

It has been shown[28] that for the case of chain initiation at the wall the following equation obtain

$$\frac{2\lambda}{\epsilon r}\,\gamma m_0 + \alpha\bar{n} = \frac{\pi^2 D}{r^2}\,\bar{n} \qquad (13)$$

$\bar{n}$ is the average concentration of chain carriers, λ is the mean free path, r the radius of a spherical reaction vessel, ϵ the chain breaking efficiency of the wall, γ the ratio of surface to volume of the vessel, m_0 the rate of chain initiation per unit surface, α the velocity coefficient of chain branching and D the diffusion coefficient. This equation is a good approximation of the exact diffusion equation for the steady state and for the usual case that $\lambda/\epsilon r \ll 1$.[28]

$\pi^2 D/r^2$ will be replaced by $k_7/[M]d^2$ and $2\lambda/\epsilon r$ will be replaced by $k/[M]d$ where $[M]$ is the total concentration.

The concentration of formaldehyde in the gas phase reaches a maximum determined from the relative rates of aldehyde forming and destroying reactions. It is given by

$$[\mathrm{HCHO}]_{\mathrm{max.}} = \frac{k_2}{2k_4}\,[\mathrm{CH_4}] \qquad (14)$$

From equation (13) and the reaction mechanism I to IX

$$\frac{kk_1}{[\mathrm{M}]d^2}\,[\mathrm{HCHO}]_{\mathrm{max.}}[\mathrm{O_2}] + \frac{k_4k_5k_8[\mathrm{HCHO}]_{\mathrm{max.}}[\mathrm{O_2}]^2}{k_6(k_5[\mathrm{O_2}] + k_9[\mathrm{HCHO}]_{\mathrm{max.}})}\,[\mathrm{OH}] = \frac{k_7}{[M]d^2}\,[\mathrm{OH}] \qquad (15)$$

whence, for $k_9[\mathrm{HCHO}]_{\mathrm{max.}} \ll k_5[\mathrm{O_2}]$, the rate of methane oxidation for the steady state is given by

$$-\frac{\mathrm{d}[\mathrm{CH_4}]}{\mathrm{d}t} = \frac{k_1k_2{}^2k}{2k_4}\,\frac{[\mathrm{CH_4}]^2[\mathrm{O_2}]}{k_7 - (k_2k_8/2k_6)[\mathrm{CH_4}][\mathrm{O_2}][M]d^2} \qquad (16)$$

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(24) Newitt and Gardner, *Proc. Roy. Soc.* (London), **A154** 329 (1936).

(25) (a) Stephens, THIS JOURNAL, **50**, 2523 (1928); (b) Grün, *Ber.*, **53**, 987 (1920).

(26) Ubbelohde, *Proc. Roy. Soc.* (London), **A152**, 378 (1935).

(27) This accounts for the peroxides isolated by Mondain-Monval, and Quanquin [*Ann. Chim.*, **15**, 309 (1931)] and others.

(28) Von Elbe and Lewis, THIS JOURNAL, **59**, 970 (1937).

Equation (16) shows that if the negative term in the denominator is small compared with k_7 the rate should be independent of the diameter of the vessel. This has been reported[29] for ethane–oxygen mixtures at low pressures (a few mm.) and at about 600° in silica vessels etched with hydrofluoric acid, the latter apparently having the effect of producing a surface of more or less uniform and also enhanced catalytic activity.[29,30] It appears that under these conditions the negative term, which is strongly dependent on pressure, is small. On the other hand, experiments on methane at 650° and at much higher pressures (atmospheric) show a decrease of the reaction rate on decreasing the dimensions of the vessel (packing).[14a] This is consistent with equation (16).

If, in a given vessel at constant temperature and pressure, the mixture composition is changed, equation (16) indicates a maximum reaction rate for a mixture containing between 50 and 66.7% methane in oxygen, the former percentage corresponding to a minimum of the denominator and the latter percentage to a maximum of the numerator. At atmospheric pressure and 447°, Bone and Allum[7b] found that a mixture containing 66.7% methane reacts faster than mixtures containing 50 or 75% methane. Intermediate points were not recorded.

Equation (16) shows that the reaction rate depends on a power of the methane concentration exceeding 2 and on a power of the oxygen concentration exceeding 1, depending on the magnitude of the negative term in the denominator compared with k_7. This is borne out by the experiments of Fort and Hinshelwood[10b] at 467° and pressures ranging from 300 to 600 mm.

The nature of the surface enters into the coefficients k_1 and k. Since the surface is likely to undergo imperceptible changes during the reaction, the rate should be erratic and unpredictable as is the general experience in untreated vessels.[31]

Concerning the explosive reaction it would be inconsistent to follow Semenoff's[32] suggestion of "degenerate" explosions for hydrocarbons since his suggestion becomes plausible only if an active intermediate of long lifetime were formed, reacting independently of the main chain reaction. No compelling reason for the suggestion is seen in the apparently continuous acceleration of the rate curves up to the inflection point since the steady-state treatment given in this paper would give the same type of curve on considering the consumption of the reactants. The condition for explosion is found to be

$$\frac{k_4k_5k_8[O_2]^2[HCHO]_{\text{max.}}}{k_6(k_5[O_2] + k_9[HCHO]_{\text{max.}})} = k_7/[M]d^2 \qquad (17)$$

It may be surmised that the actually observed explosion limit is somewhat affected by the rate of heat liberation, that is, the reaction rate. This would explain why the explosion limits depend somewhat upon the nature of the surface[20c,33] which enters into the coefficients k and k_1.

The sum of the energies of activation of reactions II and VIII is most probably larger than the energy of activation of reaction VI; the sum of the energies of reactions II and IX is larger than the sum for reactions IV and V. $[M]$ is equal to the sum of the concentrations $[CH_4] + [O_2] + [X]$, where $[X]$ is the concentration of any foreign gas. Combining equations (14) and (17) and substituting temperature functions, one obtains

$$([CH_4] + [O_2] + [X])\frac{[CH_4][O_2]^2}{[O_2] + K'e^{-A'/T}[CH_4]} = \frac{K}{d^2}e^{A/T} \qquad (18)$$

The ignition temperature should increase with decreasing vessel dimensions. This has been confirmed by experiments at 1 atmosphere pressure.[33,34]

Equation (18) reduces approximately to

$$\log P = (A/T) + B \qquad (19)$$

A and B being constants; the experimental curves have often been expressed by equations of this type.[14c,31]

If foreign gas, such as argon, is added to the mixture without affecting the concentrations of CH_4 and O_2 (that is, total pressure is increased), the ignition temperature should decrease. This has been found experimentally.[35] If part of the combustible mixture is replaced by foreign gas leaving the sum of the concentrations the same, the ignition temperature should increase. This also has been observed.[36] Moreover, if helium is substituted for argon, the ignition temperature is higher,[36] corresponding to the larger

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(29) Sadownikow, *Phys. Z.* (U. S. S. R.), **4**, 735 (1933).

(30) Kowalsky, Sadownikow and Tschirkow, *ibid.*, **1**, 451 (1932).

(31) Sagulin, *Z. physik. Chem.*, **B1**, 275 (1928); compare reference 14c with Neumann and Serbinow, *Phys. Z.* (U. S. S. R.), **1**, 536 (1932).

(32) N. Semenoff, "Chemical Kinetics and Chain Reactions," Oxford University Press, Oxford, Eng., 1934.

(33) Mason and Wheeler, *J. Chem. Soc.*, 2079 (1922).

(34) Taffanel and Floch, *Compt. rend.*, **157**, 469 (1913).

(35) Neumann and Serbinow, *Phys. Z.* (U. S. S. R.), **4**, 433 (1933).

(36) Naylor and Wheeler, *J. Chem. Soc.*, 2456 (1931).

value of the diffusion coefficient which enters into k_7 and, therefore, K.

If the ratio of methane to oxygen is changed, leaving the sum of the concentrations constant, the ignition temperature should pass through a minimum for a mixture ratio $CH_4:O_2 < 1:1$. Only if the term $K'e^{-A'/T}[CH_4]$ in the denominator of (18) were negligible would this minimum occur at a ratio 1:1. The larger this term is the more the minimum is shifted to leaner mixtures. Since the term becomes larger toward higher temperatures, mixtures diluted with foreign gas should exhibit a shift of the minimum ignition temperature to smaller ratios of $CH_4:O_2$ than is found in the undiluted mixture. In fact, at 1 atmosphere total pressure the minimum ignition temperature for undiluted mixtures has been found at a ratio of about 1:2, whereas using argon as diluent (O_2:A the same as $O_2:N_2$ in air) the minimum is at a ratio 1:3.6.[36] If the ignition temperature is increased still further by replacing argon by helium, the minimum is at a ratio 1:4.[36]

If the size of the vessel is decreased, thus increasing the ignition temperature, the minimum again shifts toward leaner mixtures.[36]

If the total pressure is increased, thus lowering the ignition temperature, the minimum shifts toward richer mixtures.[20c]

According to equation (17), it should be possible to induce explosions by the addition of formaldehyde in excess of $[HCHO]_{max}$. Smaller amounts should not lower the ignition temperature although they should decrease the induction period. Actually, formaldehyde added in amounts of 1 to 2% substantially lowers the ignition temperature;[20c] in amounts of about 0.027% practically no lowering is observed, but the induction period is markedly shortened.[36] That $[HCHO]_{max.}$ is smaller than 1% appears from the fact that in the non-explosive oxidation of CH_4, formaldehyde is found only in traces.[7b]

Higher Hydrocarbons.—The mechanism of the oxidation of higher hydrocarbons consists of the following reactions and the former reactions IV to IX.

Initiation

$$RCHO + O_2 \xrightarrow{\text{surface}} RCO(OOH) \xrightarrow{\text{surface}} RCOO + OH \qquad \text{I}$$

Hydrocarbon oxidation chain

$$OH + RCH_3 = RCH_2 + H_2O \qquad \text{II}$$

$$RCH_2 + O_2 = RCH_2OO \qquad \text{III}$$

$$RCH_2OO = R'CHO + CH_3O \xrightarrow{O_2} CO + H_2O + OH \qquad \text{X}$$

Peroxide branching

$$RCH_2OO + RCHO = (RCH_2O - OC(OH)R) \xrightarrow{O_2} 5OH \qquad \text{XI}$$

Degradation reaction

$$RCHO + OH = H_2O + RCO \xrightarrow{O_2} CO + H_2O + R'CO \xrightarrow{O_2} \ldots$$

$$CO + H_2O + CH_3CO \xrightarrow{O_2} HCHO^* + CO + OH \qquad \text{XII}$$

The condition for explosion is now found to be

$$\underbrace{\frac{k_2k_{11}}{k_{10}}[RCH_3][Ad]_{max.}}_{\text{Peroxide branching}} + \underbrace{\frac{k_4k_5k_8[O_2]^2[Ad]_{max.}}{k_6(k_5[O_2] + k_9[HCHO]_{max.})}}_{\text{Peracid branching}} = k_7/[M]d^2 \qquad (20)$$

where $[Ad]_{max.}$ is now the total maximum aldehyde concentration and equals

$$[Ad]_{max.} = \left(\frac{2k_4}{k_{12}} - 1\right)[HCHO]_{max.} = \frac{k_2}{2k_4}\left(\frac{2k_4}{k_{12}} - 1\right)[RCH_3] \qquad (21)$$

As before, the nature of the surface has been found to influence somewhat the explosion limits.[14c,20]

Since the peracid branching term is small at low temperatures and moderate pressures, the peroxide branching term must be large in order to fulfill the explosive condition (20). Since the radical R-OO is considered to have a long lifetime at low temperatures, the peroxide branching term is largely dominated by reaction X and is proportional to $Te^{A/T}[RCH_3]^2$. This term increases with decreasing temperature, tending toward infinity, thus accounting for the pronounced explosivity toward lower temperatures. The reason the reaction becomes non-explosive again at still lower temperature may be due to the greater stability toward oxidation of the condensation product in reaction XI and a gas phase chain breaking process involving the combination of two R-OO radicals. That the reaction becomes non-explosive at low pressures can be seen from equation (20). Thus, in a qualitative way, the peninsula shape of the explosion region and the maximum in the reaction rate may be accounted for.

It is reasonable to assume that the activation energies of the reactions in question are more or less independent of the length of the paraffin molecule so that the temperature limit of the peninsula is approximately the same for all higher paraffins.

Equation (20) in combination with (21) shows that for richer mixtures the explosion limit should be shifted toward lower pressures, which has been observed.[20] Decreasing the vessel diameter narrows the explosion region;[14c,20] if this is carried to the extreme by packing, the reaction, explosive or non-explosive, is entirely suppressed.[14a] Since, due to the intensity of peroxide branching, the concentration of excited formaldehyde becomes rather high, it is understandable that the luminescence should become pronounced ("cool" flames). Simultaneously the induction periods become very short[20] (see Fig. 1). If aldehyde is added to the mixture, branching becomes large immediately. In ethane, where the peninsula is weakly developed, addition of 1 to 2% of acetaldehyde brings out the peninsula phenomenon sharply and reduces the induction period prior to explosion from hours to seconds.[20c]

If the aldehyde added exceeds $[\mathrm{Ad}]_{\mathrm{max.}}$, the explosion region should widen progressively with increasing amounts. Also, the nature of the aldehyde should make little difference. These facts have been observed.[20]

If the energy of activation of reaction II exceeds that of reaction IV the value of $[\mathrm{Ad}]_{\mathrm{max.}}$ should increase toward higher temperatures. This explains the decreased effect of aldehyde on the position of the explosion limits toward higher temperatures.[20,37]

At higher temperatures the peracid branching term becomes predominant, and the ignition characteristics of higher hydrocarbons approach those of methane. The limits are generally lower, which is consistent with the larger $[\mathrm{Ad}]_{\mathrm{max.}}$ as compared with $[\mathrm{HCHO}]_{\mathrm{max.}}$ Comparing the explosion regions of methane[20c] and also isobutane[20b] with those of normal paraffins, it may be estimated that peroxide branching predominates up to about 400° whereas peracid branching predominates above about 500°.

That addition of foreign gas without altering the concentrations of the reactants produces the same effect as it does in methane, namely, lowers the ignition temperature, is shown in hexane–air and hexane–oxygen explosions.[20b] Likewise, if a part of the mixture is replaced by foreign gas, the ignition temperature is increased.[20b]

Experiments are available on the effect of mixture composition on the minimum ignition pressure in the region of predominant peracid branching as defined above. According to equation (20) toward lower temperatures the minimum should again shift from a mixture ratio of less than 1:1 to 1:1. At about 680° a minimum ignition pressure was found for a pentane–oxygen mixture having a ratio about 1:2.[31] At a considerably lower temperature, 480–520°, a minimum was found for an ethane–oxygen mixture having a ratio 1:1.[14c]

Studies of reaction rates are not apt to lead to simple relationships since branching of one type or another appears over the whole temperature range. As long as peroxide branching is predominant the equation for the reaction rate (same as equation (16) with peroxide branching term replacing peracid branching term) indicates that the most reactive mixture should be far on the rich side, >2:1. Measurements show that the rate is still increasing for a 2:1 mixture.[7a]

Summary

It is pointed out that there are certain shortcomings in existing theories which are overcome in the proposed theory. The concept of chain initiation *via* aldehyde is seen to require discussion of aldehyde oxidation. A chain mechanism consistent with experimental facts and chemical plausibility is described. The chain mechanisms of aldehyde and hydrocarbon oxidation are linked to each other and combined with a modified form of Pease's mechanism for higher hydrocarbons. Plausible relations between the high pressure oxidation of methane and ethane and the chemistry of peroxides are discussed. From this, a branching reaction involving alkyl peroxides and aldehydes which is operative predominantly at low temperatures is shown to be plausible chemically. It is called "peroxide branching" to distinguish it from "peracid branching" operative predominantly at high temperatures. The mechanisms of primary aldehyde forming reactions and secondary non-chain reactions are discussed. It is shown that kinetic facts concerning the slow reaction and explosion limits of methane are consistent with the scheme; that certain phenomena exhibited by higher hydrocarbons at relatively low temperatures (ex-

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(37) This also explains why in ethane–oxygen mixtures, Bone and Hill[7a] observed an explosion induced by 1% acetaldehyde, whereas Steacie and Plewes[7c] did not. The former worked at 316° and the latter at 452° (*cf.* Townend and Chamberlain).[20c]

plosion peninsula, maximum in the reaction rate, "cool" flames) can be described by peroxide branching; and that peracid branching can describe the explosion limits of higher hydrocarbons at high temperatures.

PITTSBURGH, PA. RECEIVED SEPTEMBER 11, 1936

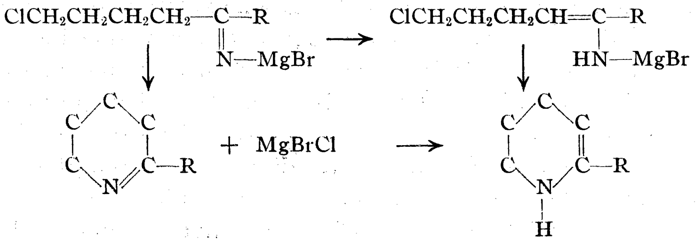
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Synthesis of Some New Alpha-Substituted Tetrahydropyridines and Piperidines[1]

BY RICHARD SALATHIEL, J. MARVIN BURCH AND R. M. HIXON

A general method for the preparation of α-substituted tetrahydropyridines has been developed, a preliminary report of which was presented by Starr and Hixon,[2] who reported the preparation of α-phenyltetrahydropyridine. This preparation followed the general plan of the method used by Craig, Bulbrook and Hixon,[3] who reported the preparation of α-substituted pyrrolines by a modification of Cloke's reaction.[4] This paper extends this synthesis to the preparation of other compounds in this series, and to the preparation of the corresponding piperidines.

The reactions involved are first the reaction of a Grignard reagent with δ-chlorovaleronitrile to form the mixed magnesium bromide salt of a δ-chlorobutylketimine, $Cl(CH_2)_4CM + RMgBr \longrightarrow ClCH_2CH_2CH_2CH_2{-}CR{=}NMgBr$, and second the closing of the ring which is accomplished by replacing the ether in the reaction mixture with xylene and raising the temperature. Expressing this reaction by equations completely analogous to those proposed by Craig, Bulbrook and Hixon,[3] two possible mechanisms are shown.



Experimental Part

δ-Chlorovaleronitrile, b. p. 118–121° (25 mm.), was prepared as described by Starr and Hixon.[2]

α-Phenyltetrahydropyridine.—A Grignard reagent was prepared from 4.86 g. of magnesium, 34.5 g. of bromobenzene and 160 cc. of ether. A solution of 23.5 g. of δ-chlorovaleronitrile in 25 cc. of ether was added dropwise, as the reaction mixture was stirred and refluxed. The addition product, a heavy viscous colorless liquid, separated from the solvent. The ether was removed by distillation from an oil-bath, the volume in the flask being kept constant by the addition of xylene. When the temperature in the flask reached 130–135°, the liquid addition product quickly changed to a solid, semi-crystalline, yellow mass. Heating just sufficient to reflux the xylene was continued for an hour. The material was cooled and hydrolyzed, using 130 cc. of hydrochloric acid (sp. gr. 1.10). The xylene layer was separated and extracted again with hydrochloric acid. The acid solution was extracted with 20 cc. of petroleum ether to remove residual xylene, then made strongly basic with sodium hydroxide and extracted with ether. The ether extract was dried and fractionated. There was collected at 142–150° (20 mm.) 21 g. of a nearly colorless oil, which turns brown quickly on exposure to air. The yield is 66% of the theoretical.

The hydrochloride, precipitated from aqueous acetone, melted at 86–87° as reported by Gabriel[5] but when dried in a current of warm air the melting point becomes 152–153°. Other derivatives, the picrate, m. p. 181.5°, and the mercuric chloride–hydrochloride double salt, m. p. 165–166°, were prepared.

α-(*p*-Chlorophenyl)-tetrahydropyridine.—A Grignard reagent prepared from 2.43 g. of magnesium, 21.1 g. of *p*-chlorobromobenzene and 125 cc. of ether, was added to a solution of 11.8 g. of δ-chlorovaleronitrile. A procedure similar to that for α-phenyltetrahydropyridine yielded 9.5 g. of a colorless base boiling at 165° (13 mm.) which crystallized in the receiver, m. p. 54°. The yield is 49% of the theoretical.

A picrate, m. p. 177–178°, was crystallized from an alcohol solution. A mercuric chloride–hydrochloride double salt, m. p. 133–135°, a chloroplatinate, m. p. 192°, and a hydrochloride, m. p. 215–217°, were prepared from aqueous solutions.

Anal. Calcd. for $C_{11}H_{12}ClN{\cdot}HCl$: N, 6.09. Found: N, 6.19, 6.15.

α-(*p*-Tolyl)-tetrahydropyridine.—A Grignard reagent prepared from 2.5 g. of magnesium turnings, 21 g. of *p*-bromotoluene and 120 cc. of ether was treated with 11.7 g. of δ-chlorovaleronitrile. The product was obtained by a procedure similar to that for α-phenyltetrahydropyridine. The major portion of the 9 g. of the product distilled over at 145° (13 mm.). The yield is 52% of the theoretical.

The following derivatives were prepared: chloroplati-

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[1] Supported in part by grants from the Rockefeller Fluid Research Fund and from the Industrial Science Research Funds of the Iowa State College.

[2] Starr and Hixon, THIS JOURNAL, **56**, 1595 (1934).

[3] Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931).

[4] Cloke, *ibid.*, **51**, 1174 (1929).

[5] Gabriel, *Ber.*, **41**, 2012 (1908).

nate, yellow needles from water, m. p. 186–187°; mercuric chloride–hydrochloride double salt, crystallized from water, m. p. 119.5°; picrate, yellow needles from alcohol, m. p. 178–179°; hydrochloride, crystallized from water solution, m. p. 137–137.5°.

Anal. Calcd. for $C_{12}H_{15}N \cdot HCl \cdot H_2O$: N, 6.15. Found: N, 6.10, 6.15.

In an oven at 100° the hydrochloride salt loses water and the melting point changes to 175–177°.

Anal. Calcd. for $C_{12}H_{15}N \cdot HCl$: N, 6.68. Found: N, 6.56, 6.61.

α-Cyclohexyltetrahydropyridine.—A Grignard reagent was prepared from 6 g. of magnesium turnings, 33 g. of chlorocyclohexane and 200 cc. of ether. A solution of 21.5 g. of δ-chlorovaleronitrile was added dropwise to the reagent and a viscous heavy liquid precipitated out. Following the usual procedure 7 g. of a light yellow oil, which darkens on exposure to air, boiling at 118–125° (17 mm.) was separated. The yield is 23% of the theoretical.

Anal. Calcd. for $C_{11}H_{19}N$: N, 8.48. Found: N, 8.50.

The hydrochloride, m. p. 222–224°, was prepared by passing hydrogen chloride gas into the free base and washing the resulting crystals with acetone. It loses hydrogen chloride slowly on standing in air.

α-(*n*-Butyl)-tetrahydropyridine.—To a Grignard reagent prepared from 4 g. of magnesium, 22 g. of *n*-butyl bromide and 170 cc. of ether, 15 g. of δ-chlorovaleronitrile was added dropwise. A liquid addition product separated out. The ether was replaced by xylene, the temperature raised and the resulting product hydrolyzed as in the α-phenyl preparation. The acid solution was made basic with sodium hydroxide and steam distilled. The distillate was made acid and concentrated by vacuum distillation, and then made basic with sodium hydroxide and extracted with ether. The dried ether extract was fractionated. The yield of a light yellow oil, boiling at 195–200°, which darkens quickly in contact with air, was 4 g. (22% of the theoretical).

Anal. Calcd. for $C_9H_{17}N$: N, 10.07. Found: N, 10.18, 10.00.

The hydrochloride decomposes easily, losing hydrogen chloride in air. The yellow crystalline chloroplatinate, m. p. 156°, was prepared from water solutions.

Anal. Calcd. for $(C_9H_{17}N)_2H_2PtCl_6$: C, 31.38; H, 5.27; Pt, 28.49. Found: C, 31.8; H, 5.32; Pt, 28.3.

α-Phenylpiperidine, in 6.5 g. yield, was prepared as described by Gabriel[5] by reduction of 9 g. of α-phenyltetrahydropyridine with tin and hydrochloric acid. It was characterized by the crystalline hydrate, m. p. 60–61°, and the hydrochloride, m. p. 200–201°.

α-(*p*-Chlorophenyl)-piperidine.—α-(*p*-Chlorophenyl)-tetrahydropyridine, 7 g., was reduced by refluxing with 60 cc. of hydrochloric acid (sp. gr. 1.10) and an excess of granulated tin for three hours. The reaction mixture was made basic with sodium hydroxide and steam distilled. The distillate was made acid with hydrochloric acid and concentrated by vacuum distillation. The hydrochloride salt crystallized out, and after recrystallization the yield was 5.3 g., m. p. 259–260°.

Anal. Calcd. for $C_{11}H_{14}ClN \cdot HCl$: N, 6.04. Found: N, 6.09, 6.02.

The base was freed from 4.7 g. of the hydrochloride with sodium hydroxide solution, extracted with ether and dried over sodium sulfate. The ether solution was fractionated, yielding 3.8 g. of a nearly colorless oil, boiling at 145° (8 mm.), which crystallized, on cooling in an ice-bath, m. p. 16°.

The chloroplatinate melted at 221° with decomposition.

α-(*p*-Tolyl)-piperidine.—A 6-g. portion of the α-(*p*-tolyl)-tetrahydropyridine was hydrogenated by refluxing for three hours with 80 cc. of hydrochloric acid (sp. gr. 1.10) and an excess of granulated tin. The reaction mixture was made basic, using a large excess of sodium hydroxide, and steam distilled. The distillate was made just acid with hydrochloric acid and concentrated by vacuum distillation to 50 cc. From this the base was set free with sodium hydroxide and extracted with ether. The dried ether extract was fractionated, yielding 5 g. of a nearly colorless oil boiling at 135° (8 mm.).

The hydrochloride, m. p. 209–210°, was prepared by passing hydrogen chloride gas into the free base and washing the resulting crystals with acetone.

Anal. Calcd. for $C_{12}H_{17}N \cdot HCl$: N, 6.62. Found: N, 6.71, 6.58.

α-Cyclohexylpiperidine.—A solution of 2.5 g. of α-cyclohexyltetrahydropyridine in 40 cc. of hydrochloric acid (sp. gr. 1.10) was refluxed with an excess of granulated tin for four hours. A separation procedure similar to that used for α-(*p*-tolyl)-piperidine yielded 1.5 g. of a pale yellow oil boiling at 135° (35 mm.).

The hydrochloride, prepared by passing hydrogen chloride gas over the base and washing the resulting crystals with acetone, melted sharply but not quite completely at 197–198°. It was apparent that there was a higher melting product present. Repeated crystallization from water of a rather large amount of the salt yielded a small amount melting at 250°. These two bodies are probably position isomers.

Anal. Calcd. for $C_{11}H_{21}N \cdot HCl$: N, 6.88. Found: N, (product melting at 197–198°) 6.90, (product melting at 250°) 6.91.

α-*n*-Butylpiperidine.—A solution of 1.8 g. of α-(*n*-butyl)-tetrahydropyridine in 20 cc. of hydrochloric acid (sp. gr. 1.10) was refluxed with an excess of granulated tin for three hours. By a separation procedure similar to that for α-(*p*-tolyl)-piperidine 1.5 g. of product, b. p. 185–192°, was obtained.

The hydrochloride, crystallized from water, melted at 185–186°. Löffler and Plöcker[6] reported 181–182° for this constant.

However, Winterfeld and Holschneider[7] reported 186–187°.

Anal. Calcd. for $C_9H_{19}N \cdot HCl$: N, 7.89. Found: N, 7.89, 7.84.

Summary

A satisfactory and convenient method for preparation of α-substituted tetrahydropyridines has been demonstrated.

The yields of the aromatic substituted com-

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[6] Löffler and Plöcker, *Ber.*, **40**, 1323 (1907).

[7] Winterfeld and Holschneider, *Ann.*, **499**, 109 (1932).

pounds are notably superior to those of the aliphatic and cycloparaffinic substituted compounds prepared.

The α-substituted tetrahydropyridines can be reduced easily to the corresponding piperidines with tin and hydrochloric acid.

The following new compounds have been prepared and suitable derivatives reported: α-*n*-butyltetrahydropyridine, α-cyclohexyltetrahydropyridine, α-cyclohexylpiperidine, α-(*p*-tolyl)-tetrahydropyridine, α-(*p*-tolyl)-piperidine, α-(*p*-chlorophenyl)-tetrahydropyridine and α-(*p*-chlorophenyl)-piperidine.

Ames, Iowa Received March 13, 1937

[Contribution from the Research Laboratory of Armour and Company]

The Preparation and Cracking of High Molecular Weight Nitriles

By A. W. Ralston, H. J. Harwood and W. O. Pool

Introduction

The present work was undertaken with the object of producing from high molecular weight fatty acids, straight chain aliphatic compounds containing less than thirteen carbon atoms per molecule. It was thought that a mixture of compounds containing only straight chains might be obtained if a fatty acid derivative which contained no oxygen were subjected to a cracking process similar to that used in the petroleum industry. The present paper is a report of the preparation and cracking of high molecular weight aliphatic nitriles and the partial identification and separation of the resulting compounds.

In undertaking a study of the cracking of high molecular weight nitriles a satisfactory method was essential for preparing such nitriles in considerable quantities from acids. The ordinary method of amide dehydration by means of agents such as phosphorus pentoxide or phosphorus oxychloride was not to be considered because of the expense of the reagents.

The pyrolysis of amides to produce nitriles in varying yields has been reported by several authors.[1] Weidel and Ciamician[2] obtained capronitrile by passing a mixture of ammonia and caproic acid vapor over red hot pumice. Mitchell and Reid[3] noted the formation of small amounts of nitriles incidental to the preparation of amides by passing ammonia through acids at 160–190°. These authors state that no amide was obtained from either palmitic or stearic acid and very little from lauric acid under their conditions.

Since lower amides are partially converted to nitriles upon distillation it seemed probable that stearamide with a high boiling point might be completely converted to nitrile in this manner. Accordingly, stearamide was distilled at atmospheric pressure. The distillate was found to consist of a mixture of stearonitrile and stearic acid together with some unchanged amide. Evidently the water formed by the dehydration of one molecule of amide had served to hydrolyze a second molecule. The ammonium stearate thus formed decomposed at the temperature of the distillation to ammonia and acid. The condition may be expressed by the following equilibria

$$\mathrm{RCOOH} + \mathrm{NH_3} \overset{\text{I}}{\rightleftarrows}$$

$$\mathrm{RCOONH_4} \underset{+\mathrm{H_2O}}{\overset{\overset{\text{II}}{-\mathrm{H_2O}}}{\rightleftarrows}} \mathrm{RCONH_2} \underset{+\mathrm{H_2O}}{\overset{\overset{\text{III}}{-\mathrm{H_2O}}}{\rightleftarrows}} \mathrm{RCN}$$

In view of the above result, it seemed probable that stearonitrile could be prepared from stearic acid by heating the acid to a sufficiently high temperature in a stream of ammonia. The ammonia would serve to force reaction I to the right and also to sweep out water as it was formed in reactions II and III. This procedure was carried out and was found to produce stearonitrile in excellent yields.

Two methods were used for the cracking of nitriles. The first consisted in passing the nitrile vapors through a glass tube packed with various catalysts maintained at temperatures of 450 to 600°. The second method was to heat the material in a closed vessel to a temperature of approximately 420°. This procedure gave higher yields than the first method and for this

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[1] Wöhler and Liebig, *Ann.*, **3**, 249 (1832); Boehner and Andrews, This Journal, **38**, 2503 (1916); Boehner and Ward, *ibid.*, **38**, 2505 (1916); Hurd, Dull and Martin, *ibid.*, **54**, 1974 (1932).

[2] Weidel and Ciamician, *Ber.*, **13**, 84 (1880).

[3] Mitchell and Reid, This Journal, **53**, 1879 (1931).

reason was used to produce most of the "cracked fractions" dealt with in this paper. There was no qualitative difference between the products obtained by the two methods.

A study of cracked material boiling from 100 to 275° showed that it consisted of straight chain nitriles and hydrocarbons, both saturated and unsaturated.

In separating the nitriles from the hydrocarbons two general methods were used; the first depended on chemically altering one or the other of the two classes of compounds, the second employed only the difference in physical properties as a basis of separation. It is apparent that the second method, in which both the nitriles and hydrocarbons are separated and recovered in an unchanged condition, is the more desirable of the two. Two obvious ways of separating nitriles from hydrocarbons consist in hydrolyzing the nitriles to alkali soluble acids or in hydrogenating them to acid soluble amines. Separation by hydrolysis has been accomplished satisfactorily, while work on separation by hydrogenation is in progress. Attempts to separate nitriles from hydrocarbons without chemical reactions of the compounds have thus far depended on the differences in solubilities in various solvents and on differences in adsorption of the nitriles and hydrocarbons on silica gel.

Experimental

The Distillation of Stearamide.—Twenty grams of stearamide (m. p. 108–109°) was distilled from an ordinary distilling flask at atmospheric pressure. The temperature of the vapor was 340°. The fumes were alkaline to moist litmus paper. From the distillate, which weighed 17 g., there were isolated 7.5 g. of stearic acid of m. p. 65.5–68°, 6.1 g. of stearonitrile of m. p. 41.5–42.5° and 1.0 g. of stearamide of m. p. 105–106.5°.

The Preparation of Stearonitrile.—The apparatus is shown in Fig. 1. The reaction flask A was constructed from a 500-cc. Claisen flask. The length of the catalyst D was 30 cm. The total length of the catalyst tube was 70 cm. Stearic acid was placed in A and heated to the desired temperature by means of an electric heater. A stream of ammonia was passed through B. The mixture was so heated that the vapor did not rise above point C, about 15 cm. above the level of the liquid. Excess ammonia, together with water vapor and small amounts of acid, passed up through the catalyst which was maintained at a temperature of approximately 400° by means of the furnace E. The fused aluminum oxide catalyst (6 mesh)[4] used served only to convert into nitrile the small amount of acid carried over by the gas stream. Without the catalyst this acid condensed in the cooler portions of the system in the form of the ammonium salt, thereby plugging the tubes. Temperatures were read with thermocouples J and K. The water was condensed in F and collected in G. Exhaust gases were removed through I.

The apparatus was charged with 284 g. of stearic acid (m. p. 68–69°) and heating was started. When the temperature reached about 150° the ammonia was passed in. By means of the heater the temperature was increased to 330° at which point it was maintained during the course of the experiment. Heating was continued for a total of six hours. The ammonia rate was such that an excess was always present. The crude material in flask A weighed 261 g. and contained 2.2% of stearic acid as determined by titration. The receiver G contained 8.5 g. of mixed amide and nitrile which was discarded.

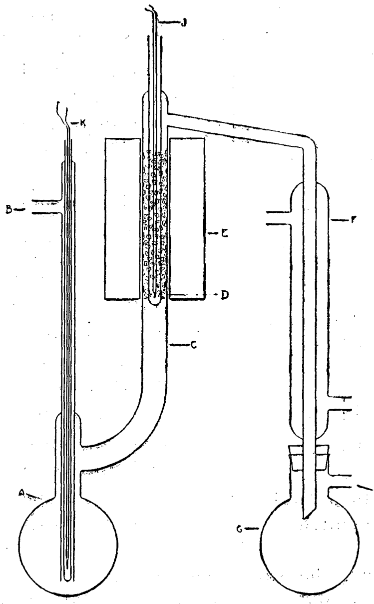

Fig. 1.—Apparatus for preparation of nitriles.

The nitrile was distilled at atmospheric pressure through a 50-cm. Vigreux column. The column was insulated and had an external heater. The nitrile had a boiling range of 352–360°, with about 75% distilling at 356–358°. The distillate weighed 234 g. and contained 3.8% of acid. This corresponds to a yield of 85%. To purify the nitrile further, it was washed with a hot, dilute solution of potassium hydroxide in 50% alcohol, then with hot water until neutral to phenolphthalein. After one crystallization from slightly dilute alcohol, the stearonitrile weighed 206 g., m. p. 41–42°. Pure stearonitrile melts at 42.5–43.0° (corr.).

Vapor Phase Cracking of Nitriles.—The apparatus used was a glass tube (2.5 cm. in diameter) packed with a catalyst and heated by an electric furnace. Temperatures were measured by a thermocouple imbedded in the catalyst. Nitriles of acids obtained from lard were vaporized at a uniform rate and passed over the catalyst in a stream of nitrogen or ammonia gas. The vapors were then con-

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[4] Obtained from the Aluminum Ore Company, East St. Louis, Illinois.

densed and the percentage of material boiling below 275° was determined by distillation. The catalysts used were glass, pumice, aluminum oxide on charcoal, fused aluminum oxide, copper on fused aluminum oxide, and iron on fused aluminum oxide. No evidence was obtained that runs using any one catalyst led to the formation of compounds not present in products obtained when other catalysts were used. Under the same conditions, the yield of cracked material, as measured by the percentage of the total product which boiled below 275°, varied with the nature and age of the catalyst. Fused aluminum oxide gave the highest yield. The uncondensed gases consisted of about half unsaturates, the remainder being saturated hydrocarbons and hydrogen.

Liquid Phase Cracking of Nitriles.—Mixed nitriles, boiling above 275° (1846 g.), made from acids (neutral equivalent of 290.0) obtained from garbage grease were placed in the steel pressure vessel B shown in Fig. 2. The pressure vessel was then heated by a gas flame. When the temperature of the nitriles had reached 330°, as measured by a thermocouple inserted in well C, the valves D and E were closed. After nineteen minutes, the pressure, which was indicated by gage F, was 90 pounds (6 atm.) and the temperature was 415°. Heating was discontinued and the temperature was allowed to drop below 275°. Then the valve E was opened gradually until the pressure had dropped to zero. Heat was applied and all cracked material having a boiling point below 275° was distilled through the water-cooled condenser G. Then valve E was closed and the cycle was repeated. From time to time, additional nitriles were introduced into the pressure vessel through the inlet A until a total of 5538 g. of nitriles had been used. After twenty cracking cycles had been completed, the distillate amounted to 4412 g. (79.7%). The residue in the cracking vessel was a thick, black oil. This residue weighed 550 g. (9.9%). The loss due to uncondensed gases was 576 g. (10.4%) by difference. The distillate was washed with a silver nitrate solution to remove hydrogen cyanide which was always formed. Some of the lower nitriles were removed by this procedure, and the remaining material weighed 4180 g.

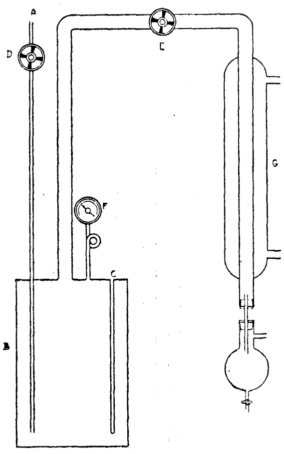

Fig. 2.—Apparatus for cracking nitriles.

Table I

Distillation of Cracked Fraction

Fraction	Weight	Boiling range, °C.	% of total	Nitrogen, %
1	405	30–105	9.7	..
2	609	105–150	14.6	3.54
3	957	150–200	22.9	4.06
4	1019	200–250	24.4	3.65
5	431	250–275	10.3	2.82
Residue	759	>275	18.1	..

The results obtained upon distillation of the 4180 g. of cracked material are shown in Table I.

Identification of Acids Obtained by Hydrolysis of Cracked Fraction.—A sample of miscellaneous cracked fraction (boiling range 100–275°) obtained by the vapor phase cracking of nitriles of acids obtained from lard over various catalysts was hydrolyzed by means of alcoholic potassium hydroxide. The acids obtained were converted into ethyl esters, hydrogenated using platinum catalyst and fractionated.[5] The curve for the second distillation is given in Fig. 3. The S-shaped curves are due to incomplete hydrogenation. The unsaturated esters have higher refractive indices but slightly lower boiling points than the corresponding saturated esters. Hence, an "S" occurs on the distillation curve instead of the usual plateau, due to a slight fractionation of the unsaturated compound from the saturated. Fraction 9 had an iodine number of 5.1.

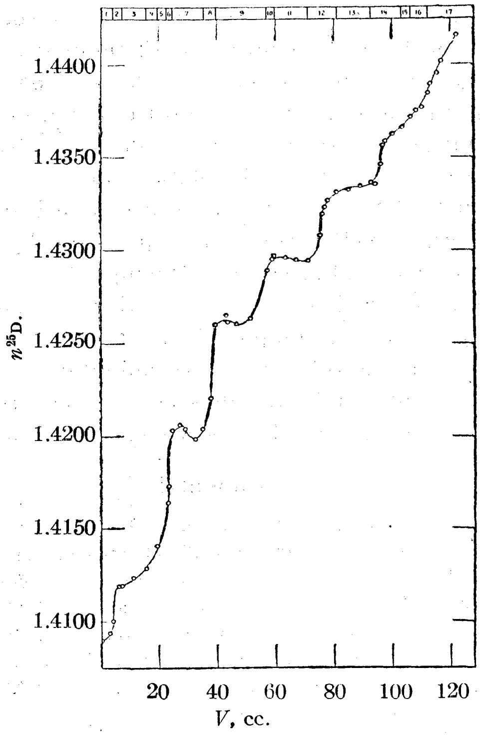

Fig. 3.—Distillation of ethyl esters. Fractions indicated at top.

A 3 to 4 g. sample from each of fractions 1, 3, 7, 9, 11, 13, and 15, Fig. 3, was saponified. The acids obtained were converted into 2-alkylbenzimidazoles according to the procedure of Pool, Harwood and Ralston.[6] The melting points of these derivatives and mixed melting points with derivatives of known acids are given in Table II

Estimation of the Amounts of Nitriles in Cracked Fractions.—The amounts of nitriles present in several cracked fractions were approximated by hydrolyzing the nitriles and weighing the resulting acids. Fifteen grams of acids

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[5] A 75-cm. column having a 10-mm. inside diameter and a Chromel wire spiral packing was used in all the fractionations in this paper.

[6] Pool, Harwood and Ralston, This Journal, **59**, 178 (1937).

TABLE II

MELTING POINTS OF 2-ALKYLBENZIMIDAZOLES

Source of acid	M. p. (corr.), °C.	Mixed m. p., °C.
Fraction 1	153.0–154.0	158–160
Caproic	163.0–163.5	
Fraction 3	135.0–136.0	136.0–136.5
Heptylic	137.5–138.0	
Fraction 7	142.5–143.0	143.0–143.5
Caprylic	144.5–145.0	
Fraction 9	136.5–137.5	138.5–139.0
Pelargonic	139.5–140.5	
Fraction 11	125.5–126.0	125.5–126.0
Capric	127.0–127.5	
Fraction 13	110.5–111.5	110.5–112.5
Undecylic	114.0–114.5	
Fraction 15	104.0–105.0	105.5–106.5
Lauric	107.5	

was obtained from 100 g. of a 30–130° fraction; similarly, 35 g. from a 100–220° fraction; and 37 g. from 100 g. each of 140–160° or 100–275° fraction.

Fractionation of the Hydrocarbons Obtained from Cracked Fraction.—Distillation curves for hydrocarbons obtained from a cracked fraction are given in Figs. 4 and 5. The curve shown in Fig. 4 was obtained by the distillation of a sample of hydrocarbons boiling below 125°. These hydrocarbons were obtained by cracking nitriles of acids obtained from cottonseed oil in a steel vessel under pressure and without a catalyst. The hydrocarbons were purified by washing with water,[7] passing over silica gel, and finally drying with sodium wire. The hydrocarbons were fractionated three times. The fractions were treated with sodium wire after each distillation in order to completely remove traces of nitriles.

The curve shown in Fig. 5 was obtained by the distillation of hydrocarbons from a sample of miscellaneous cracked fractions (boiling range 100–275°). These cracked fractions were prepared by the vapor phase cracking of nitriles of acids obtained from lard over various catalysts. The nitriles were removed from the hydrocarbons by hydrolysis to alkali soluble acids. The hydrocarbons (iodine number 135) were hydrogenated in the vapor phase to an iodine number of 6.8 using a nickel–chromium catalyst. The curve is for the third fractionation. Here, also, the S curves were due to incomplete hydrogenation.

In Table III are given iodine numbers and percentages of unsaturated hydrocarbons for various fractions of the distillation shown in Fig. 4. One double bond per molecule was assumed in calculating these percentages. Qualitative tests for acetylenic linkages were negative.

TABLE III

Fraction	B. p., °C.	Iodine No.	% unsatd. hydrocarbon
1	<37	102.8	28.3% Pentene
4	60–63	154.5	51.1% Hexene
5	63–66	142.3	47.1% Hexene
6	66–69	103.7	34.2% Hexene
7	69–72	89.5	29.6% Hexene
11	93–96	130.3	50.4% Heptene
12	96–99	100.6	38.8% Heptene

Separation of Nitriles from Hydrocarbons by Hydrolysis.—A cracked fraction (2500 g.) having a boiling range of 100–220°, together with 1600 g. of water and 400 g. of sodium hydroxide, was placed in a rocking autoclave and heated to 200°. The time required to attain this temperature was thirty minutes. The heat was then turned off, but the rocking was allowed to continue for an additional ninety minutes during which time the temperature dropped to 100°. The bomb was cooled, the contents were transferred to a separatory funnel, and the lower aqueous layer was drawn off after settling for one hour. The alkaline salt solution was steam distilled for several hours in order to remove a few grams of hydrocarbons which had remained suspended in the aqueous layer. The clear solution was then acidified with concentrated hydrochloric acid, and the resulting upper layer of fatty acids was separated and distilled. The acids weighed 890 g. and had a boiling range of 190° at 760 mm. pressure to 140°

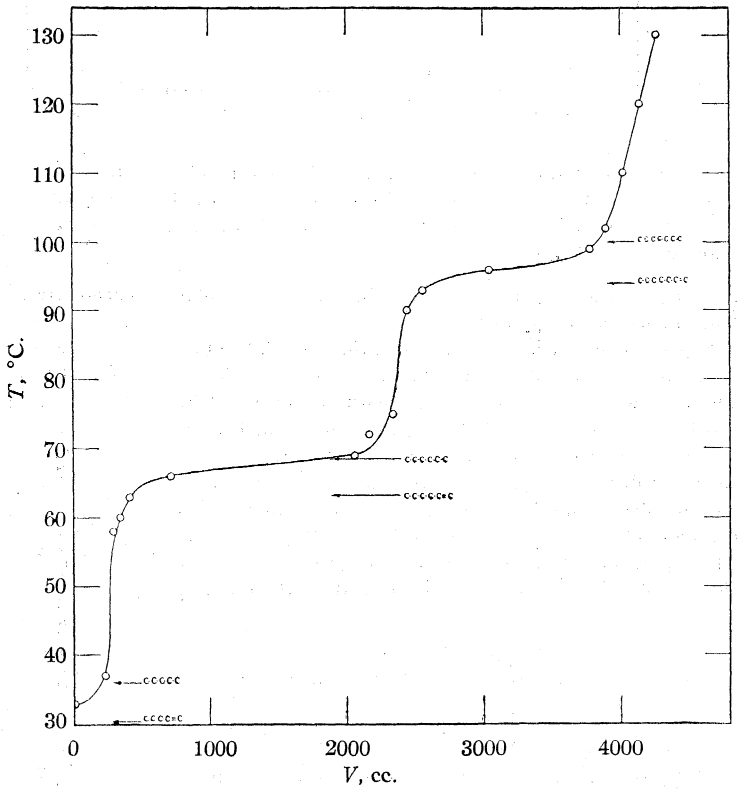

Fig. 4.—Distillation of hydrocarbons. Arrows indicate b. p. of respective compounds.

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(7) Acetonitrile, b. p. 79–81.5°, was isolated from the water washings.

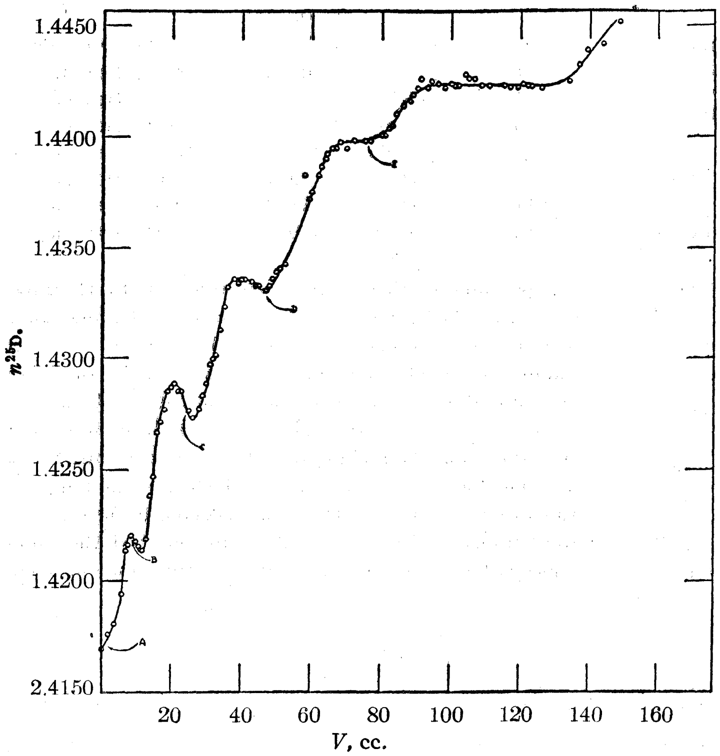

Fig. 5.—Distillation of hydrocarbons: A corresponds to 125° − b. p. of *n*-octane; B to 151° − b. p. of *n*-nonane; C to 174° − b. p. of *n*-decane; D to 195° − b. p. of *n*-undecane; E to 214° − b. p. of *n*-dodecane.

at 5 mm. pressure. The last few drops of the distillate had a molecular weight of 178.

Separation of Nitriles from Hydrocarbons by Solvents.—A sample of cracked fraction having a boiling range of 140–160° was washed three times with concentrated hydrochloric acid, then with water, and finally with dilute potassium hydroxide solution. The cracked fraction was then distilled under vacuum over phosphorus pentoxide. The distillate contained 0.04% fatty acid calculated as caproic and had a nitrogen content of 0.942 g. per 25 cc. The separation of the nitriles from the hydrocarbons by the use of different solvents was studied by the following method: 25 cc. of the cracked fraction was pipetted into a glass-stoppered 50-cc. graduated cylinder. Twenty-five cubic centimeters of the solvent to be tested was added. After thorough shaking, the mixture was allowed to separate into layers at room temperature and the volume of each layer was recorded. An aliquot from each layer was taken with a capillary pipet and the amount of nitrogen was determined. Some typical results are given in Table IV.

TABLE IV

SEPARATION OF NITRILES FROM HYDROCARBONS BY SOLVENTS

Solvent	Upper layer Vol., cc.	Upper layer N. g.,	Lower layer Vol., cc.	Lower layer N, g.
100.0% MeOH[a]	13.3	0.049	36.7	0.884
93.8% MeOH[a]	14.8	.088	35.2	.856
93.8% MeOH	9.5	.083	40.5	.860
70.6% MeOH	20.7	.457	29.3	.478
65.2% MeOH[b]	18.0	.239	82.0	.703
70.4% EtOH	19.7	.379	30.3	.563
95.6% Phenol[c]	9.5	.002	42.0	.939

[a] Separation of layers occurred at −77°. [b] Three volumes of solvent were used to one volume of cracked material. [c] Separation occurred at 4°. The volume of the phenol solution used was 26.5 cc.

Adsorption of Nitriles by Silica Gel.—The apparatus used is shown in Fig. 6. Solutions of nitriles were introduced at A and were forced downward through the column of silica gel[8] by nitrogen gas under a pressure of 8 cm. The nitrogen entered the system at B. In some cases the adsorbed material was removed by heat supplied by the electric furnace C. The temperature was ascertained by means of thermocouple D enclosed in a glass tube extending to the bottom of the silica gel. A solution of Eastman valeronitrile in petroleum ether (boiling range 33–50°), containing 24.40 g. of nitrile in a liter of solution, was passed through 16.5 g. of silica gel and the effluent liquid was received in fractions. Results are given in Table V.

A solution of lauronitrile in petroleum ether, containing 16.742 g. of nitrile in a liter of solution, was passed through 18.5 g. of silica gel. Results are given in Table VI.

Separation of the Nitriles from the Hydrocarbons in Cracked Fractions by Adsorption in Silica Gel.—Twenty-five cubic centimeters of cracked fraction similar to that used in the experiments on separation by solvents, was allowed to flow onto a column of silica gel weighing 58 g. The entire 25 cc. was adsorbed or held by capillarity.

TABLE V

ADSORPTION OF VALERONITRILE BY SILICA GEL

Fraction	Vol., cc.	N content, g.	Valeronitrile content, g.	Valeronitrile per 100 cc., g.
Blank	50	0.0003	0.0018	0.003
1	100	.0005	.0030	.003
2	30	.0001	.0006	.002
3	9	.0008	.0048	.053
4	11	.0227	.1346	1.222
5	7	.0290	.1720	2.460

TABLE VI

ADSORPTION OF LAURONITRILE BY SILICA GEL

Fraction	Vol., cc.	N content, g.	Lauronitrile content, g.	Lauronitrile per 100 cc., g.
1	50	0.0004	0.0052	0.010
2	50	.0003	.0039	.008
3	50	.0003	.0039	.008
4	50	.0004	.0052	.010
5	50	.0198	.2560	.512
6	50	.0516	.6672	1.336
7	20	.0242	.3129	1.565

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[8] The silica gel was the "Intermediate Activated" grade of the Silica Gel Corporation, Baltimore, Md.

Forty-five cubic centimeters of petroleum ether (boiling range 33–50°) was allowed to flow over the silica gel in order to wash off the hydrocarbons from the cracked fraction. The effluent liquid was received in a Kjeldahl flask, and the petroleum ether was removed by evaporation on a steam-bath. The hydrocarbons remaining in the flask had an approximate volume of 20 cc. and contained 0.0004 g. of nitrogen. Ammonia gas was then passed over the silica gel, which became warm and the temperature of the column was further increased by heat from the surrounding furnace until a final temperature of 400° had been attained. The heat caused a displacement of 2.0 cc. of water and 6.1 cc. of nitriles. The nitriles were washed thoroughly with hydrochloric acid to remove ammonia preparatory to analysis for nitrogen. The 6.1 cc. contained 0.861 g. of nitrogen.

Discussion

While the pyrolytic decomposition of amides to yield nitriles and water is well known, the simultaneous dehydration and hydration to yield nitriles and acids has not been reported previously. Apparently, in the case of stearamide, the nitrile and acid are formed in equimolecular amounts. Experiments not reported indicate that a similar reaction occurs in the case of lauramide.

The method described here for the preparation of nitriles is distinguished from older methods in that it is carried out in the liquid phase and in the absence of catalysts and produces almost theoretical yields of nitriles. The method has been applied to a variety of higher fatty acids and has been carried out on a very much larger scale in iron vessels.

Sufficient evidence has been presented to indicate the composition of the material produced by the cracking of high molecular weight nitriles. Certain conclusions in regard to the total composition of the cracked material are based on data obtained from restricted fractions. The cracked material consisted of a mixture of nitriles and hydrocarbons. Saturated and unsaturated compounds were present in approximately equal amounts in certain hydrocarbon fractions. That the mixture contained only straight chains is indicated by the occurrence of definite plateaus or breaks in the distillation curves of the hydrocarbons and of esters derived from the nitriles (Figs. 3, 4 and 5). In the volume–refractive index curves (Figs. 3 and 5) the breaks are accentuated by the presence of small amounts of unsaturated compounds. In the case of the hydrocarbons these breaks occur at points corresponding to the boiling points of the straight chain compounds. This would not be the case if branched chains had been present in other than very small amounts. The fractionated esters were further identified by means of derivatives. These derivatives showed the presence of straight chain nitriles containing from six to twelve carbon atoms in the particular fraction of cracked material which was used. Since hydrogen cyanide and acetonitrile were identified, it is reasonable to assume that nitriles and hydrocarbons containing from one to seventeen carbon atoms are produced by the cracking process. There was no indication that any particular chain length was predominant.

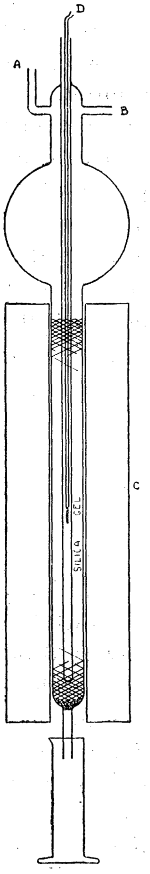


Fig. 6.—Adsorption apparatus.

Because of the similarity in physical properties of nitriles and hydrocarbons, considerable difficulty was experienced in attempting to separate them. Separation by fractional distillation was out of the question as the boiling point of any certain nitrile would have practically coincided with the boiling point of some hydrocarbon of greater chain length. Separation was possible by the preferential solubility of the nitriles in certain solvents from which the nitriles could be recovered unchanged. In Table IV, it is seen that the addition of 25 cc. of 93.8% methyl alcohol to 25 cc. of cracked fraction caused the formation of two layers having volumes of 9.5 cc. and 40.5 cc. Since the smaller layer does not decrease appreciably upon being washed with water, the solvent accounts for 25 cc. of the larger layer. If the solvent were removed by washing with water, 15.5 cc. of cracked fraction containing 0.860 g. of nitrogen would remain. By solvents it is thus possible to separate the cracked fraction into two parts, one of which has a nitrogen percentage 6.3 times as great as that of the other. Such a process would never yield pure nitriles and pure hydrocarbons in one operation, but repeated extractions could be made to give nitriles or hydrocarbons of almost any desired purity. Separation by adsorption appears to be preferable to separation by solvents. From

Table V, fractions 1 and 2 (130 cc.) contained only 0.004 g. of valeronitrile. The original nitrile solution contained 3.172 g. of valeronitrile in 130 cc. Therefore, 16.5 g. of silica gel adsorbed 3.168 g. of nitrile before adsorption ceased to be complete. This amount is equivalent to 19% of the weight of the silica gel. The nitrile can be displaced from the silica gel by means of hot water. By use of the data in Table VI it can be shown that silica gel will adsorb 18% of its weight of lauronitrile from a hydrocarbon solution before small amounts of nitrile appear in the effluent liquid. In the last of the adsorption experiments it is shown possible to remove practically all of the nitriles from a cracked fraction and to recover it after adsorption by heating the silica gel. The original 25 cc. of cracked material contained 0.942 g. of nitrogen, of which 0.861 g. was accounted for in the material removed from the silica gel by heating. Less than 1% of the nitriles was not adsorbed.

Summary

1. The decomposition of high molecular weight amides by heat has been shown to cause a simultaneous hydration and dehydration which leads to the formation of almost equal amounts of acids and nitriles.
2. A non-catalytic method has been developed for preparation of high molecular weight nitriles from fatty acids and ammonia.
3. High molecular weight nitriles have been cracked in the liquid and vapor phases to yield straight chain hydrocarbons and nitriles.
4. Methods have been described which permit the separation of nitriles from hydrocarbons.

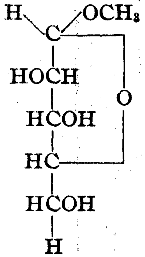
Chicago, Illinois Received November 16, 1936

[Contribution from the National Institute of Health, U. S. Public Health Service]

Crystalline Alpha-Methyl-*d*-arabinofuranoside[1]

By Edna M. Montgomery and C. S. Hudson

A new crystalline methyl *d*-arabinoside, which is shown in the accompanying article by Jackson and Hudson to be the alpha form of *d*-arabinofuranoside,[2] has been isolated from the mixture of substances that is obtained by the reaction of *d*-arabinose and methyl alcohol containing hydrochloric acid under mild conditions of glycoside formation. This reaction is accompanied by a double reversal of the sign of optical rotation, as has been reported by previous investigators.[3] The authors were able to crystallize the new furanoside, the rotation[4] of which (+123 in water) is opposite in sign to that of the sugar itself (−105) and to those of its alpha (−17) and beta (−245) methyl pyranosides, by stopping the reaction at its point of highest positive rotation. The substance crystallizes in well formed, clear prisms and the yield is about 9%. Its fast rate of hydrolysis in aqueous acid conforms with the behavior of known furanosides of aldoses. From the present knowledge of the rotation of this alpha form it appears safe to conclude that the rotation of beta-methyl-*d*-arabinofuranoside, a substance now unknown, will be found to be strongly in the levo direction.



Alpha-methyl-*d*-arabinofuranoside, $[\alpha]^{20}_{D}$ +123

Experimental

The removal of solvents and the drying of sirups and crystals were carried out at 25–27° in desiccators supplied with calcium chloride and soda lime and evacuated by a pump. When constant weights were desired the higher vacuum of an oil pump was used for final dryings. The hygroscopic character of the furanoside crystals and the high humidity of the summer atmosphere during the work made it advisable to perform many of the manipulations in dry air. We used a cabinet of 55 × 39 × 43 cm. dimen-

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Report of the isolation of this compound was included in a paper entitled "The Oxidation of Alpha and Beta Forms of Methyl *d*-Arabinoside and Methyl *d*-Xyloside," presented by E. L. Jackson and C. S. Hudson at the Pittsburgh meeting of the American Chemical Society, Sept. 7–11, 1936.

(3) Baker and Haworth, *J. Chem. Soc.*, **127**, 365 (1925); Levene, Raymond and Dillon, *J. Biol. Chem.*, **95**, 699 (1932).

(4) Throughout this article the rotations are specific rotations at 20° for sodium light.

sions constructed of copper with a glass top and a removable end with strip felt closure, the other end being provided with two openings of 13 cm. diameter into which long rubber gloves[5] were fitted with adhesive tape.

Crystallization of α-Methyl-*d*-arabinofuranoside.—One hundred grams of finely powdered and sieved *d*-arabinose, rotation −105 in water, was agitated at 20° with 4 liters of anhydrous methyl alcohol containing 29.2 g. of hydrochloric acid (0.2 normal). Complete solution was obtained after thirty minutes and the observed rotation was strongly to the left, −65. On standing at 20° the solution became non-reducing after four and one-half hours and its specific rotation was then +24. On further standing the rotation increased in the dextro direction, reached a maximum of +45 after seventeen hours, and then receded until after forty-two hours it had reversed its sign and become −17. The new furanoside was obtained in greatest yield if the reaction was stopped when the rotation reached its maximum positive value. The acid was removed with silver oxide, the excess silver with hydrogen sulfide, the solution was concentrated *in vacuo* to 200 cc. (bath at 40°), transferred to a liter bottle, further concentrated to a thick sirup and finally dried overnight in an evacuated desiccator. The sirup was extracted six times at room temperature (25°) with 400-cc. portions of anhydrous ether, using a shaking machine for forty-five minutes for each extraction. At this point extraction with warm ether dissolved a relatively small amount of material, the rotation of which was much lower than that of the readily soluble portion. The ether was removed at the pump from the combined cold extractions (bath at 35°) leaving a sirup weighing about 23 g. of specific rotation +100 to +105, as tested on samples dried to constant weight. An ethyl acetate solution of this sirup which was kept at 5° crystallized spontaneously after two months. In later preparations the seeded sirup crystallized to a cake in two days. It was stirred with 25 cc. of ethyl acetate and filtered to remove sirupy material. The crystalline glycoside, dried under reduced pressure for several hours, weighed 11.5 g. and rotated +118 in water. It was recrystallized from 50 cc. of warm ethyl acetate by slowly cooling to 5° over a period of four to five hours. After three recrystallizations a crop of well formed, transparent prisms was obtained which was dried to a constant weight of 6.1 g., rotation +123 in water ($c = 1.20$). Recrystallization did not change this value. An additional 3.8 g. of pure material was obtained from the mother liquors; total yield, 9%. It did not reduce Fehling's solution but was readily hydrolyzed by acids to give a reducing solution. It melted at 65–67° in a closed tube, solidifying to colorless crystals on cooling. By warming 1.0 g. of the furanoside in 200 cc. of ether, which had been dried with sodium, a solution of about 0.80 g. was obtained which deposited crystals after two days at 5°. These were dried to a constant weight of 0.35 g. and showed a rotation of +123 ($c = 1.24$) in water, m. p. 65–67°. The glycoside was not difficult to prepare in pure anhydrous condition in small quantities, *i. e.*, 0.5 to 1.0 g. It is quite hygroscopic and is extremely soluble in water, methyl, ethyl, propyl and amyl alcohols, soluble in ethyl acetate and slightly soluble in ether.

Anal. Calcd. for $C_5H_9O_4(OCH_3)$: C, 43.88; H, 7.38; OCH_3, 18.91. Found: C, 44.08; H, 7.50; OCH_3, 18.63.

Rates of Hydrolysis of the Three Methyl-*d*-arabinosides.—The rates were measured on 2% solutions of the glycosides at 98° by polarimetric observations after rapid cooling to 20°, using 0.05 *N* aqueous hydrochloric acid with each pyranoside, and 0.01 *N* acid with the furanoside, which is more readily hydrolyzed. The reactions follow the unimolecular course and the coefficient $k = 1/t \log ((r_0 - r_\infty)/(r - r_\infty))$, expressed in minutes and decimal logarithms, has the following values: α-methyl-*d*-arabinopyranoside, 0.0032; β-methyl-*d*-arabinopyranoside, 0.0032; α-methyl-*d*-arabinofuranoside, 0.0068. Assuming the rate to be proportional to the acidity, the coefficient is about 0.00064 for the pyranosides in 0.01 *N* acid and it is seen that the furanoside is hydrolyzed about ten times faster than the pyranosides.

The authors are indebted to Dr. R. M. Hann and Dr. W. T. Haskins for the carbon, hydrogen and methoxyl determinations and to Dr. O. E. May of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, for the supply of calcium gluconate from which the *d*-arabinose was prepared.

Summary

A new crystalline arabinoside, alpha-methyl-*d*-arabinofuranoside, specific rotation in water +123, m. p. 65–67°, has been isolated. Its rate of hydrolysis in aqueous acid is about ten times that of either alpha- or beta-methyl-*d*-arabinopyranoside.

WASHINGTON, D. C. RECEIVED APRIL 5, 1937

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[5] Obstetrical gloves, furnished by dealers in medical supplies, are very satisfactory.

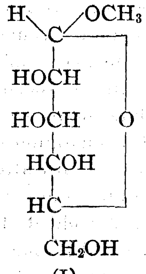
[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Studies on the Cleavage of the Carbon Chain of Glycosides by Oxidation. A New Method for Determining Ring Structures and Alpha and Beta Configurations of Glycosides[1]

BY ERNEST L. JACKSON AND C. S. HUDSON

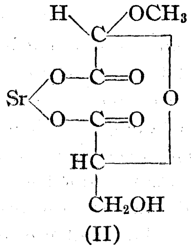
The oxidation of alpha-methyl-*d*-mannopyranoside (I) with barium hypobromite has been shown by us[2] to remove carbon atom 3 and to oxidize the alcohol groups at carbon atoms 2 and 4 to carboxyl groups, producing a dibasic acid which was isolated as the crystalline strontium salt (II). This salt could be prepared also through oxidation of the mannoside with periodic acid followed by oxidation of the product, the dialdehyde (III), with bromine water kept neutral with strontium carbonate. Inasmuch as this cleavage type of oxidation should be applicable to a large number of glycosides, it offered a new method for the proof of ring structures, provided the products from the various glycosides could be obtained in crystalline condition suitable for structural studies. The present article reports our progress in the development of the method as pertains to the methylaldohexosides and the methylaldopentosides.

The method consists in the oxidation of the glycoside with periodic acid in aqueous solution at 20° followed by the oxidation of the dialdehyde, after isolation, with bromine water in the presence of a metallic carbonate selected to yield a crystalline salt of the dibasic acid, the proof of the structure of which, in the case of the glycosides here studied, discloses the ring structure of the parent glycoside.[3] Important confirmatory evidence in the case of some structures is obtained by the measurement of the quantity of periodic acid consumed, as will be illustrated later.



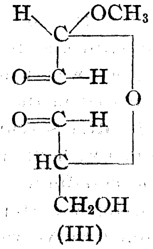
(I)

α-Methyl-*d*-manno-pyranoside



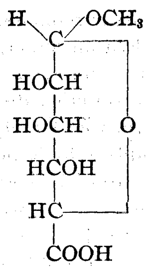
(II)

Strontium D′-methoxy-D-hydroxymethyl-diglycolate



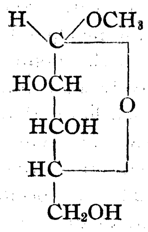
(III)

D′-methoxy-D-hydroxy-methyl-diglycolic aldehyde



(IV)

α-Methyl-*d*-mannuronide(1,5)



(V)

α-Methyl-*d*-arabino-furanoside

Inspection of the formulas shows that the same dialdehyde (III) and strontium salt (II) should be expected from all the eight possible alpha-methyl-*d*-aldohexopyranosides. The production of the same dialdehyde in the oxidation of four of these (the alpha-methyl-pyranosides of *d*-mannose, *d*-galactose, *d*-glucose and *d*-gulose) is apparent from the rotations recorded in Table I and the curves shown in Fig. 1. The dialdehyde from each of the four sources, isolated as a sirup and oxidized in the usual way, produced in yields of 65–70% the same crystalline strontium salt (II). The structure[4] of the strontium salt, particularly the presence of the *d*-glyceric acid moiety in the molecule, limits the ring of each of the four alpha-methyl-*d*-hexosides to the pyranoside(1,5) or septanoside(1,6) structure. In addition to the usually accepted evidence, two independent proofs, which exclude the septanoside ring structure and thereby

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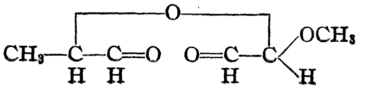
[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] Jackson and Hudson, THIS JOURNAL, **58**, 378 (1936); *Science*, **85**, 51 (1937).

[3] The proof of the structure might be accomplished also through the dialdehyde or a suitable derivative. By the periodic acid oxidation of alpha-methyl-*l*-rhamnoside of specific rotation −62.8° we have obtained, at the dialdehyde stage, a crystalline compound melting at 101–102° and showing $[\alpha]^{20}_{D}$ −143° in water. Analyses for carbon, hydrogen and methoxyl show its empirical formula to be $C_6H_{12}O_6$, corresponding to the monohydrate of the expected dialdehyde



$$CH_3-\underset{H}{C}-\underset{H}{C}{=}O\quad O{=}\underset{H}{C}-C\begin{smallmatrix}OCH_3\\H\end{smallmatrix}$$

[4] The experimental details, omitted in ref. 2, for the preparation of oxalic and *d*-glyceric acids from the strontium salt are given in the experimental part of this article.

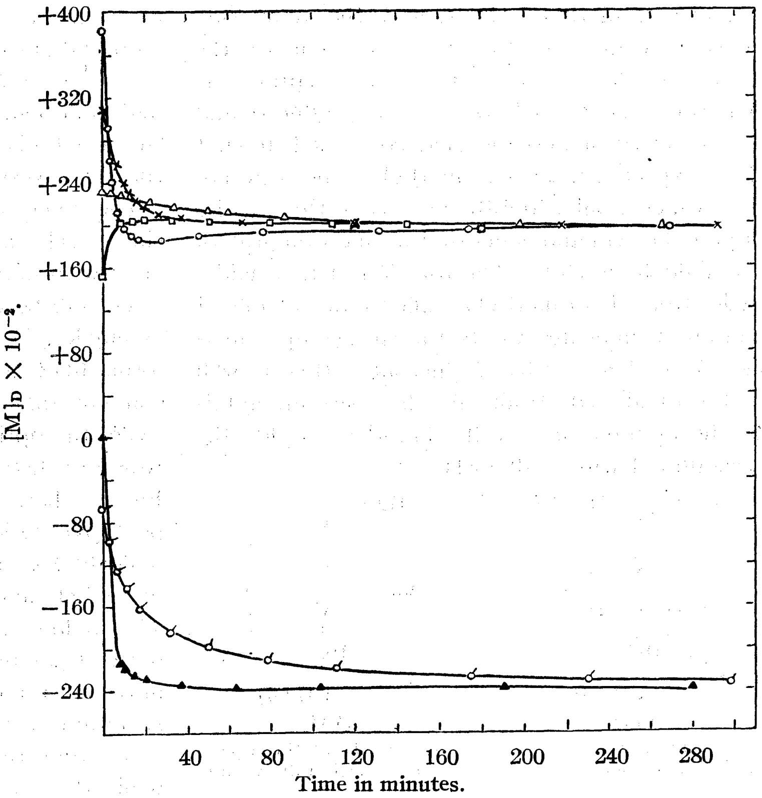


Fig. 1.—Rotatory changes during the oxidation of the methyl hexosides: ○, α-methyl-*d*-galactoside; ×, α-methyl-*d*-glucoside; △, α-methyl-*d*-guloside; □, α-methyl-*d*-mannoside; ♂, β-methyl-*d*-glucoside; ▲, β-methyl-*d*-galactoside.

limit the ring to that of a pyranoside, are provided by the present investigation. From the products of the oxidation of alpha-methyl-*d*-mannopyranoside with barium hypobromite we have prepared a crystalline brucine salt (m. p. 232°) which has been proved to be the brucine salt of alpha-methyl-*d*-mannuronide (IV). The formation of the methyl *d*-mannuronide through the oxidation of the primary alcohol group at carbon atom 6 to a carboxyl group obviously is incompatible with the 1,6-ring structure. The second proof is furnished by the preparation, through the usual oxidation reactions, of the strontium salt (II) from a new crystalline methyl-*d*-arabinofuranoside[5] (V); this proof will be presented when the oxidation of the methyl pentosides is discussed. The conclusion that the strontium salt (II) has the indicated structure is further supported by the known reactions of periodic acid;[6] the septanoside structure for an alpha-methyl-*d*-aldohexoside would be expected to consume three moles of periodic acid and yield the dialdehyde (X) (a substance which we have obtained from the alpha-methyl-*d*-pentopyranosides), whereas the alpha-methyl-*d*-aldohexosides that have been studied consume two moles of periodic acid and yield the dialdehyde (III).

The beta-methyl-*d*-aldohexopyranosides react with periodic acid in the same manner as the alpha forms, but the product (VI) is of course different since the dialdehydes from an alpha-beta pair retain the difference in configuration of carbon atom 1 that existed in the parent glycosides. Although the strontium salt in the beta series was not a crystalline compound, the barium salt (VII) crystallized quite readily and in high yield when prepared from beta-methyl-*d*-glucoside. By the same reactions as applied to the strontium salt from alpha-methyl-*d*-mannopyranoside, oxalic and *d*-glyceric acids were prepared from the barium salt; this limits the

TABLE I

PRODUCTS OF THE OXIDATION OF THE METHYL PENTOSIDES AND THE METHYL HEXOSIDES

Substance	Methyl glycoside $[\alpha]^{20}_D$	Dialdehyde[a] $[\alpha]^{20}_D$	Dibasic acid[b] $[\alpha]^{20}_D$	Strontium salt[c] $[\alpha]^{20}_D$
α-Methyl-*d*-arabinoside	− 17	+124.2	−12.7	−55.5
α-Methyl-*d*-xyloside	+154	+125.2	−12.1	−55.5
β-Methyl-*d*-arabinoside	−245	−123.7	+12.5	+55.7
β-Methyl-*d*-xyloside	− 65	−124.3	+12.2	+55.3
α-Methyl-*d*-arabinofuranoside	+123	+117.3[d]	+26.1	−53.3
α-Methyl-*d*-galactoside	+196	+120.7	+25.4	−53.5
α-Methyl-*d*-glucoside	+159	+121.1	+26.0	−52.9
α-Methyl-*d*-guloside	+120	+120.5	+25.4	−52.7
α-Methyl-*d*-mannoside	+ 79	+119.5	+26.3	−53.0
β-Methyl-*d*-galactoside	+ 1	−148.1	....	....
β-Methyl-*d*-glucoside	− 34	−150.6	+45.0	+35.9[e]

[a] D′ and L′-methoxy-diglycolic aldehydes from the methyl pentopyranosides; D′ and L′-methoxy-D-hydroxymethyl-diglycolic aldehydes from α-methyl-*d*-arabinofuranoside and the methyl hexosides. Specific rotations calculated from the final [M]D values of the oxidation solutions (Tables II and V). [b] Determined by liberating the acid (*c*, 1.2–1.6) from its pure, anhydrous strontium salt (barium salt for β-methylglucoside) with an equivalent of hydrochloric acid. [c] See Table IV, note (b) and Table VII, note (b). [d] See note (19). [e] Barium salt (*c*, 3.4).

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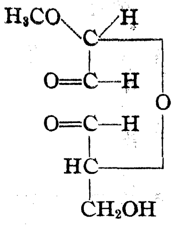
(5) Montgomery and Hudson, THIS JOURNAL, **59**, 992 (1937).

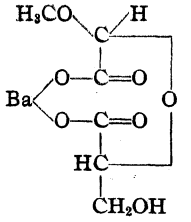
(6) Malaprade, *Bull. soc. chim.*, [5] **1**, 833 (1934); Clutterbuck and Reuter, *J. Chem. Soc.*, 1467 (1935); Fleury and Bon-Bernatets, *J. pharm. chim.*, [8] **23**, 85 (1936); Hérissey, Fleury and Joly, *ibid.*, [8] **20**, 149 (1934).

ring of beta-methyl-*d*-glucoside to the pyranoside or septanoside structure. In addition to the known evidence to exclude the septanoside structure, the dialdehyde that is produced and the quantity of periodic acid consumed are not those expected from beta-methyl-*d*-glucoseptanoside, which would doubtless consume three moles of periodic acid and generate the enantiomorph of the dialdehyde (X). The rotation of the dialdehyde from beta-methyl-*d*-galactoside (Table I and Fig. 1) indicates it to be the same compound as (VI) from beta-methyl-*d*-glucoside; this as well as the dialdehyde from all other beta-methyl-*d*-aldohexopyranosides will doubtless yield the crystalline barium salt (VII).



(VI)

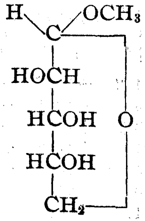
L′-methoxy-D-hydroxymethyl-diglycolic aldehyde



(VII)

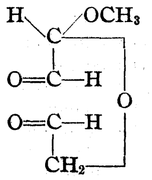
Barium L′-methoxy-D-hydroxymethyl-diglycolate

The oxidation products are named as derivatives of diglycolic aldehyde or acid; the prefixes D′ and L′ distinguish the configurations of carbon atom 1 in the products from the alpha- and beta-methyl glycosides, D′ signifying the configuration of carbon atom 1 as in alpha-methyl-*d*-mannopyranoside. The dibasic acid of specific rotation +26° from the alpha-methyl-*d*-aldohexopyranosides is named D′-methoxy-D-hydroxymethyl-diglycolic acid and that from beta-methyl-*d*-glucopyranoside, of specific rotation +45°, is named L′-methoxy-D-hydroxymethyl-diglycolic acid. The D and L symbols conform to the usual Fischer nomenclature for carbon 5 of the aldohexosides.



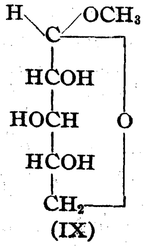
(VIII)

α-Methyl-*d*-arabinopyranoside



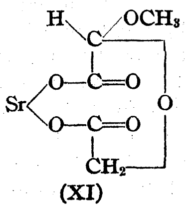
(X)

D′-methoxy-diglycolic aldehyde



(IX)

α-Methyl-*d*-xylopyranoside



(XI)

Strontium D′-methoxy-diglycolate

The oxidation of alpha-methyl-*d*-arabinopyranoside (VIII) and alpha-methyl-*d*-xylopyranoside (IX) with periodic acid should yield one and the same substance, namely, D′-methoxy-diglycolic aldehyde (X), and a similar oxidation of the beta forms likewise should be expected to produce a common dialdehyde, L′-methoxy-diglycolic aldehyde, the optical antipode of (X). The specific rotations listed in Table I and the curves in Fig. 2 show that the two pairs of methyl-*d*-pentopyranosides do indeed produce antipodal dialdehydes, the one from the alpha forms rotating +124° and that from the beta forms −124°. The dialdehyde from each of the four *d*-pentopyranosides produced, upon oxidation with bromine water and strontium carbonate, a crystalline strontium salt in about 80% yield; the salt (XI) from the two alpha forms rotated −56° while the salt from the two beta forms rotated +56°; these two salts are thus enantiomorphic forms. The methoxy-diglycolic acids from the methyl pentopyranosides, like the methoxy-D-hydroxymethyl-diglycolic acids from the methyl-aldohexopyranosides, are hydrolyzed readily in aqueous solution because of their acetal structure. The acid from the strontium salt (strontium L′-methoxy-diglycolate) prepared from beta-methyl-*d*-arabinopyranoside, when hydrolyzed and oxidized with bromine water yielded oxalic and glycolic acids, the latter identified through three crystalline derivatives (calcium glycolate, S-benzylthiuronium glycolate and *p*-bromophenacyl glycolate). Since glycolic acid contains only one alcoholic hydroxyl group, the oxygen linkage in the strontium salt must be as indicated, which proves the four parent methylpentosides to be of the pyranoside type and correlates the alpha and beta forms. Since the application of the usual oxidation reactions to a third crystalline methyl-*d*-arabinoside[5] (V) of specific rotation +123° yields a different strontium salt (II) (the one from the alpha-methyl-*d*-aldohexopyranosides, containing the *d*-glyceric acid grouping), the third methyl-*d*-arabinoside must have the furanoside structure (V) and be of the alpha configuration for carbon 1. This is the second proof, mentioned previously, for the structure of (II), (III) and (I). One observes that these oxidation results correlate the configuration of a pentofuranoside (V) and a hexopyranoside (I).

The ring structures which have been shown by these oxidation results confirm the pyranoside structures that are now accepted from methylation data; in the case of alpha-methyl-*d*-gulopyranoside and alpha-methyl-*d*-arabinofuranoside, where methylation data are lacking, the new method supplies conclusive proof for ring structures and alpha classification.

The preparation of *d*-glyceric acid from the methyl *d*-aldohexosides through either strontium D′-methoxy-D-hydroxymethyl-diglycolate or barium L′-methoxy-D-hydroxymethyl-diglycolate provides the most direct correlation of the configuration of the sugars with glyceric acid.[7] The present type of oxidation offers the possibility of improved methods for the preparation in pure condition of stereoisomers, such as *d*- and *l*-glyceric and lactic aldehydes and the corresponding acids, and of many mixed acetals for which no methods of synthesis have been known. These oxidation reactions, with periodic acid as the oxidant, appear to proceed practically quantitatively according to the following typical equations, the first of which has been proposed by Hérissey, Fleury and Joly.[6]

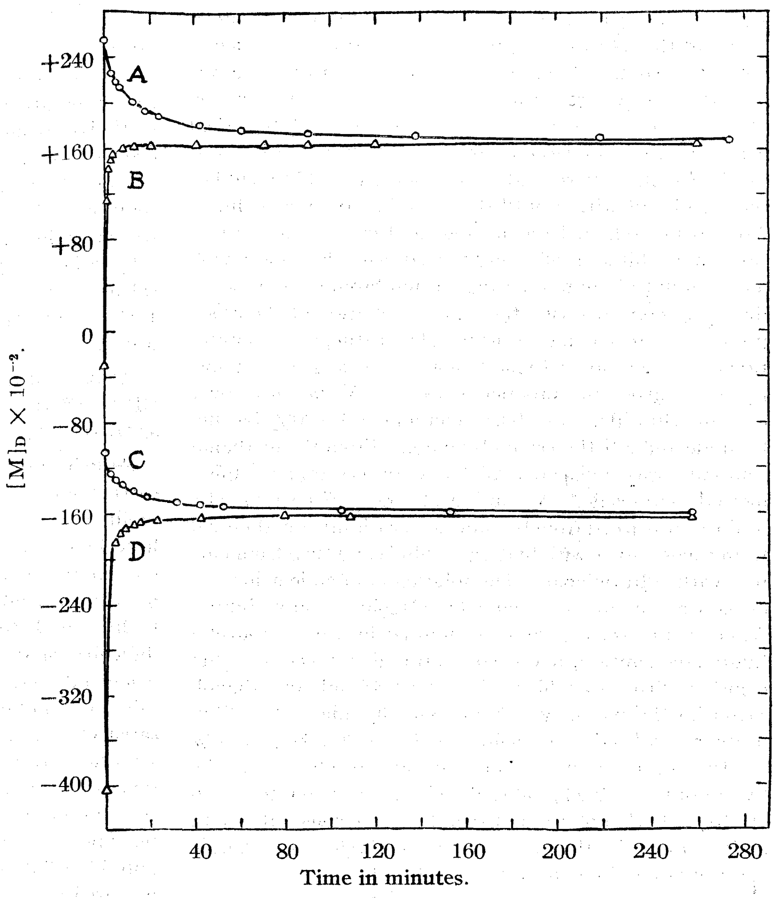
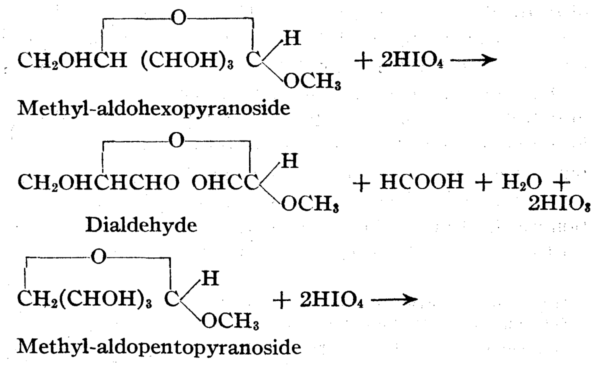


Fig. 2.—Rotatory changes during the oxidation of the methyl-pentopyranosides: (A), α-methyl-*d*-xylopyranoside; (B), α-methyl-*d*-arabinopyranoside; (C), β-methyl-*d*-xylopyranoside; (D), β-methyl-*d*-arabinopyranoside.



$$\mathrm{CH_2OH\overbrace{CH\ (CHOH)_3\ C}^{O}\begin{smallmatrix}H\\OCH_3\end{smallmatrix} + 2HIO_4 \longrightarrow}$$

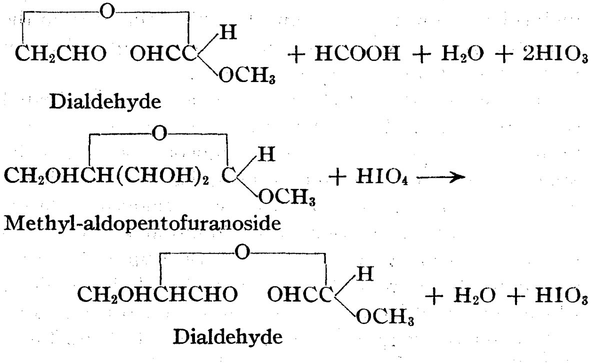
Methyl-aldohexopyranoside

$$\mathrm{CH_2OH\overbrace{CHCHO\ \ OHCC}^{O}\begin{smallmatrix}H\\OCH_3\end{smallmatrix} + HCOOH + H_2O + 2HIO_3}$$

Dialdehyde

$$\mathrm{\overbrace{CH_2(CHOH)_3\ C}^{O}\begin{smallmatrix}H\\OCH_3\end{smallmatrix} + 2HIO_4 \longrightarrow}$$

Methyl-aldopentopyranoside



$$\mathrm{\overbrace{CH_2CHO\ \ OHCC}^{O}\begin{smallmatrix}H\\OCH_3\end{smallmatrix} + HCOOH + H_2O + 2HIO_3}$$

Dialdehyde

$$\mathrm{CH_2OH\overbrace{CH(CHOH)_2\ C}^{O}\begin{smallmatrix}H\\OCH_3\end{smallmatrix} + HIO_4 \longrightarrow}$$

Methyl-aldopentofuranoside

$$\mathrm{CH_2OH\overbrace{CHCHO\ \ OHCC}^{O}\begin{smallmatrix}H\\OCH_3\end{smallmatrix} + H_2O + HIO_3}$$

Dialdehyde

Experimental

Oxidation of Alpha-Methyl-*d*-mannopyranoside with Barium Hypobromite.—To a solution of 420 g. of barium hydroxide octahydrate and 166 g. of bromine in 12 liters of distilled water at 3° was added 100 g. of pure alpha-methyl-*d*-mannopyranoside. The solution, kept in the dark at 3–7° with occasional shaking, was free from hypobromite after eight to ten days as shown by starch–potassium iodide paper. The reaction of a second portion of the same amounts of barium hydroxide and bromine was complete after about eight days. The insoluble material (70–

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[7] *Cf.* Wohl and Momber, *Ber.*, **47**, 3346 (1914); **50**, 455 (1917); Wohl and Schellenberg, *ibid.*, **55**, 1404 (1922); Freudenberg and Brauns, *ibid.*, **55**, 1339 (1922).

75 g.), apparently barium carbonate, was removed by filtration and the neutral solution was concentrated *in vacuo* to 500 ml. About 325 g. of crystalline barium bromide was separated in two crops through filtration and concentration of the filtrate *in vacuo* to 250–300 ml. The solution then was evaporated *in vacuo* to dryness; a solution of the residue in 75 ml. of warm water was poured into 2 liters of hot methanol and stirred until the precipitated gum solidified. After being refluxed for an hour and cooled, the barium salts were filtered off and washed with hot methanol. The amount of contaminating barium bromide may be reduced by concentrating the aqueous solution of the crude product *in vacuo* to a thin sirup and repeating the precipitation and extraction with methanol. The yield of the amorphous, hygroscopic product, dried at 25° *in vacuo* over calcium chloride, was 100 g. containing 15–20% barium bromide and a little barium bromate. From the methanol solutions was recovered 25–30 g. of crystalline alpha-methyl-mannoside. A solution of 250 g. of barium salts in water was freed from bromine ions with silver carbonate, from excess silver with hydrogen sulfide and then from barium with sulfuric acid. The solution of organic acids was dextrorotatory and reduced Fehling's solution only slightly. After neutralization to phenolphthalein with strontium hydroxide solution, it was concentrated *in vacuo* to a thin colorless sirup to which was added 15 ml. of ethanol. Strontium D′-methoxy-D-hydroxymethyl-diglycolate dihydrate crystallized at 5° as fine needles; yield, 80 g. or 25% on the alpha-methyl-mannoside that reacted with the hypobromite. Recrystallized twice from water to which 10–15% of ethanol was added and dried to constant weight at 105° *in vacuo*, the pure anhydrous salt showed a specific rotation[8] of −53.0° in water (*c*, 0.6).

Anal. Calcd. for $C_6H_8O_7Sr$: C, 25.74; H, 2.88; OCH_3, 11.1; Sr, 31.33. Found:[9] C, 25.74, 25.54; H, 2.93, 3.04; OCH_3, 10.9, 10.8; Sr, 31.47, 31.49.

The specific rotation of D′-methoxy-D-hydroxymethyl-diglycolic acid in water, obtained by liberating it from the pure anhydrous strontium salt with an equivalent of hydrochloric acid, was +25.5° (*c*, 1.6).

Brucine alpha-methyl-*d*-mannuronide was prepared from 16 g. of crude barium salts. After removal of the bromine ions and the barium, the aqueous solution of the organic acids was heated on the steam-bath for three hours with excess of brucine; the excess was removed by filtration followed by extraction with chloroform, and the solution was concentrated *in vacuo* to a dry sirup. The sirup was crystallized from absolute ethanol and the product, which appeared to be a mixture of several brucine salts, yielded on fractionation from 95% ethanol about 4.5 g. (12%) of nearly pure brucine alpha-methyl-*d*-mannuronide. This was recrystallized to the constant melting point of 232° (dec.) from 95% ethanol, in which it is difficultly soluble. The pure compound lost 6.1% in weight upon being dried at 105° *in vacuo* and then showed a specific rotation of −2.5° in water (*c*, 2).

Anal. Calcd. for $C_{30}H_{38}O_{11}N_2$: C, 59.77; H, 6.36; OCH_3, 15.45; N, 4.65. Found (dried at 105° *in vacuo*): C, 59.70, 59.73; H, 6.26, 6.31; OCH_3, 15.4, 15.4; N, 4.70, 4.72.

This identification of the brucine salt was confirmed by the preparation from it of crystalline potassium alpha-methyl-*d*-mannuronide.[10] The calculated potassium hydroxide was added to a solution of 10 g. of pure brucine salt in 200 ml. of water, the brucine was removed and the solution was concentrated *in vacuo* to a thin sirup, which was crystallized with the aid of ethanol. The potassium salt showed $[\alpha]^{20}\text{D}$ + 45.2° in water (*c*, 1.5), from which is calculated $[\alpha]_{5780}^{20}$ +47.1° using the dispersion coefficient[11] 1.042. Ault, Haworth and Hirst reported $[\alpha]_{5780}^{17}$ +48° in water.

Anal. Calcd. for $C_7H_{11}O_7K \cdot {}^1/_2C_2H_5OH$: K, 14.5; OR (as OCH_3), 17.3. Found: K, 14.5, 14.4; OR (calcd. as OCH_3), 16.4.

Periodic Acid.—The subsequent oxidation reactions were carried out with solutions of pure periodic acid. In some preliminary experiments in which certain alpha-methyl-hexosides were oxidized by periodic acid prepared in aqueous solution from potassium periodate and an equivalent of sulfuric acid, the yield of strontium D′-methoxy-D-hydroxymethyl-diglycolate was low, probably due to the difficulty of complete removal of potassium ions which would interfere with the crystallization of the strontium salt. Crystalline periodic acid[12] (H_5IO_6) was found more satisfactory. To avoid interference with polarimetric observations by a small precipitate which separates in oxidations with fresh solutions of the product which we used, the solutions were kept overnight or longer at 20° and filtered prior to analysis[13] and use in oxidation experiments. Suitable solutions of periodic acid in water may also be prepared from barium periodate ($Ba_3I_2O_9$). A solution of 75 g. of potassium periodate in 2500 ml. of hot distilled water was cooled cautiously to the beginning of crystallization (about 65°); to this was added a solution of 89.2 g. of pure barium acetate monohydrate in 500 ml. of cold water. It was shaken thoroughly while cooling in ice-water and then kept at 5° for about six hours. The barium periodate was filtered off, washed free from acetic acid with cold water, air-dried for two days and then at 25° *in vacuo* over calcium chloride; yield 115–120 g., containing 37.6% barium. A solution of periodic acid was prepared by shaking mechanically for one and one-half hours a suspension of 20.6 g. of powdered barium periodate in 45 ml. of distilled water to which was added *N* sulfuric acid exactly equivalent to the barium found by analysis; the filtered solution was made to 200 ml. with water.

Oxidation of the Methyl-pentopyranosides.—To 98 ml. of 0.2693 *M* aqueous periodic acid (HIO_4) solution at 20° in a 100-ml. volumetric flask was added 2.0568 g. of the pure, powdered methyl-pentopyranoside crystals. The crystals were dissolved as quickly as possible, and the solution was kept in a 20° room while the rotatory changes recorded in Table II were observed. When the rotation

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[8] Throughout the article the rotations are for sodium light and all specific rotations are at 20°.

[9] All methoxyl analyses were carried out by E. P. Clark's modified Zeisel method [*J. Assoc. Official Agr. Chem.*, **15**, 136 (1932)].

[10] Ault, Haworth and Hirst, *J. Chem. Soc.*, 517 (1935).

[11] Phelps and Hudson, THIS JOURNAL, **48**, 505 (1926).

[12] Obtained from G. Frederick Smith Chemical Co., Columbus, Ohio.

[13] All analyses for periodic acid were carried out by the arsenite method for the determination of periodic acid in the presence of iodic acid [Fleury and Lange, *J. pharm. chim.*, [8] **17**, 107 (1933)].

TABLE II

ROTATORY CHANGES DURING THE OXIDATION OF THE METHYL-PENTOPYRANOSIDES TO DIALDEHYDES[a]

2.0568 g. of methyl-pentopyranoside and 98 ml.[b] of 0.2693 *M* HIO_4 solution[c]

α-Methyl-*d*-arabino-pyranoside		β-Methyl-*d*-arabino-pyranoside		α-Methyl-*d*-xylo-pyranoside		β-Methyl-*d*-xylo-pyranoside	
Time after soln., min.	$[M]_D \times 10^{-2}$	Time after soln., min.	$[M]_D \times 10^{-2}$	Time after soln., min.	$[M]_D \times 10^{-2}$	Time after soln., min.	$[M]_D \times 10^{-2}$
0	− 28.4[d]	0	−402.9[d]	0	+252.6[d]	0	−107.5[d]
1.33	+113.0	4.42	−185.4	3.2	+224.7	2.9	−124.5
1.92	+140.6	6.83	−178.5	5.1	+218.1	5.3	−130.5
2.9	+150.2	9.3	−173.7	7	+213.0	8.1	−135.2
4	+154.4	13.1	−168.8	13	+200.3	13.4	−139.9
8	+160.2	15.4	−168.2	18	+195.4	19.1	−143.6
12.9	+162.4	23	−165.4	24.1	+190.2	31.9	−149.1
21.1	+163.1	43.1	−163.3	42.2	+182.1	42.4	−151.2
41.2	+164.0	80	−162.6	60.7	+177.8	52.8	−152.2
71	+164.0	109	−162.6	90.2	+174.4	104.6	−156.7
90	+164.0	258	−163.3	137.9	+171.6	152.8	−158.8
120	+164.0			219	+168.8	258	−160.4
260	+164.0			274	+167.6	16 hrs.	−164.2
				557	+165.4		

[a] See Fig. 2. [b] The volume of the solution, measured at 20° after completion of the reaction, was 99.8 ml. [c] Although the reaction solution was kept in a 20° room, its temperature did not remain constant, due to the heat evolved in each of the oxidation reactions. *Cf.* α-methyl-galactoside, Table V, note *c*. [d] Calcd. from the usually accepted specific rotations in water of the methyl-pentopyranosides, which are in the order listed: −17.3, −245.5, +153.9, −65.5.

ceased to change, 5 ml. of the solution was analyzed for periodic acid at the time specified in Table III; the amount found in each case corresponded approximately to the excess (5%) over two molecular equivalents added at the start. The remainder of the solution was neutralized to phenolphthalein with hot strontium hydroxide solution with care to avoid any excess. The precipitate (strontium iodate and a little strontium periodate) was filtered off and washed with cold distilled water. After the addition of 1 g. of strontium carbonate the solution[14] was concentrated *in vacuo* (bath, 50°) to about 25 ml., filtered and the concentration (bath, 40°) continued to dryness. The residue was extracted thrice with 25-ml. portions of cold absolute ethanol and thrice with 10-ml. portions. An aqueous extract (35 ml.) of the crystals insoluble in ethanol showed no optical activity, indicating the complete solution of the dialdehyde in the ethanol. The dialdehyde was recovered from the ethanol solution as a colorless sirup by distillation of the solvent *in vacuo* (bath, 40–45°); its rotation in 250 ml. of solution in water is shown in Table III. The solution then was diluted with water to 500 ml.; 38 g. of strontium carbonate and 3 ml. of bromine were added and the mixture shaken until the bromine dissolved. The mixture was kept in the dark at room temperature for about eighteen hours with frequent shaking during the first hour. Excess bromine was removed by aeration and excess strontium carbonate by filtration. The rotation of the filtrate, containing principally strontium methoxy-diglycolate and strontium bromide, is given in Table III. After the strontium carbonate was washed with cold water, the combined solution and washings were shaken with silver carbonate (about 25 g.) until free from bromine ions, and the solids were filtered off and washed with cold water. The silver was removed from the filtrate as silver sulfide, excess hydrogen sulfide was expelled by aeration and the solution was concentrated *in vacuo* (bath, 50–60°) to about 50 ml., filtered and the concentration continued to 10–15 ml., when crystals of strontium methoxy-diglycolate began to separate. After completion of crystallization in the refrigerator the crystals were filtered off and washed with about 2 ml. of cold water. A second crop was obtained by evaporating the filtrate *in vacuo* to dryness and crystallizing the sirup from about 5 ml. of water to which ethanol was added to saturation. The yield of strontium methoxy-diglycolate trihydrate (air-dried, or dried at 25° *in vacuo* over calcium chloride) was the same from each of the four methyl-pentopyranosides, 3 g. or 79%. The crude trihydrate derived from the two alpha-methyl-*d*-pentopyranosides showed a specific rotation of about −43° in water (*c*, 0.6); the trihydrate from the two beta forms rotated about +43°. The strontium salt from each of the four sources was recrystallized thrice from eight parts of distilled water, yielding needles of the trihydrate; the rotation of the anhydrous salt, dried to constant weight at 100° *in vacuo*, was then constant. The rotations and

TABLE III

CONSUMPTION OF PERIODIC ACID. ROTATIONS BEFORE AND AFTER BROMINE OXIDATION OF THE DIALDEHYDES

Methyl-pentoside	HIO_4 analysis Time, hrs.	Excess, %	Rotation[a] of sirupy dialdehyde α_D	Rotation[b] after bromine oxidation α_D
α - Methyl - *d* - arabino-pyranoside	3	4.8	+1.63	−0.65
β - Methyl - *d* - arabino-pyranoside	4	4.9	−1.64	+ .66
α - Methyl - *d* - xylo-pyranoside	8	6.1	+1.64	− .61
β - Methyl - *d* - xylo-pyranoside	16	5.3	−1.63	+ .66

[a] In aqueous solution (250 ml.); 2-dm. tube. [b] In aqueous solution (500 ml.); 2-dm. tube.

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[14] The neutral solution usually was kept overnight at 20–25° before distillation.

TABLE IV

ROTATIONS AND ANALYSES OF THE STRONTIUM SALTS FROM THE PENTOPYRANOSIDES

Methyl-pentoside	$C_5H_6O_6Sr \cdot 3H_2O$ Found,[a] % H_2O	$C_5H_6O_6Sr$[a]				
		$[\alpha]^{20}D$ in water[b]	C	H	OCH_3	Sr
Calculated values, %	17.80		24.03	2.42	12.42	35.10
α-Methyl-*d*-arabino-pyranoside	17.78	−55.5°	24.04	2.68	12.22	34.97
β-Methyl-*d*-arabino-pyranoside	17.82	+55.7°	23.92	2.56	12.20	34.91
α-Methyl-*d*-xylo-pyranoside	17.73	−55.5°	24.06	2.68	12.17	35.01
β-Methyl-*d*-xylo-pyranoside	17.79	+55.3°	23.94	2.69	12.16	35.07

[a] Dried to constant weight at 100° *in vacuo*. The anhydrous salts are quite hygroscopic. [b] C = 1.07–1.15 g. per 100 ml. of solution. At concentrations of 0.6–1.2 g. per 100 ml. the rotation, which varies with the concentration, may be expressed by the equation: $[\alpha]^{20}D = \pm 48.5° \pm 6.33\ C$, the positive sign pertaining to the salt from the β-methyl *d*-pentopyranosides.

analyses are shown in Table IV. The rotation of the dibasic acid from each of the strontium salts is recorded in Table I.

Proof of Structure.—To a solution of 15.0 g. of pure strontium salt ($C_5H_6O_6Sr \cdot 3H_2O$), derived from beta-methyl-*d*-arabinopyranoside, in 250 ml. of water, was added 98.8 ml. of N sulfuric acid and 350 ml. of 95% ethanol; after fifteen hours the strontium sulfate was filtered off and washed with cold 50% ethanol. The filtrate was concentrated *in vacuo* to about 50 ml., the solution was diluted with 50 ml. of ethanol, filtered and the concentration continued to a colorless sirup, which was taken up in water and again concentrated *in vacuo* (bath, 50°) to a thick sirup. The dextrorotatory solution of the sirup in 100 ml. of water was heated on the steam-bath for two hours; it then showed no rotation[15] in a 4-dm. tube. After dilution of the solution with water to 200 ml., 4 ml. of bromine was dissolved in it and the mixture kept in the dark at room temperature for forty-five hours. Excess bromine was removed by aeration, and the solution was neutralized to phenolphthalein with barium hydroxide solution. The precipitated barium oxalate was filtered off, washed and dried at 25° *in vacuo* over calcium chloride; yield, 6.1 g. From the barium oxalate was prepared oxalic acid dihydrate which was identified by its melting point of 99.5–101° and by titration with solutions of sodium hydroxide and potassium permanganate.

To the filtrate from the crude barium oxalate was added sufficient sulfuric acid to precipitate the barium exactly. The filtered solution was freed from bromine ions by shaking with 25 g. of silver carbonate, after which excess silver was removed as sulfide and the solution concentrated *in vacuo* to about 50 ml., filtered and the concentration continued to make exactly 25 ml. of solution, aliquots of which were used for the preparation of derivatives of glycolic acid. Calcium glycolate was prepared by neutralizing 11.5 ml. to phenolphthalein with pure calcium hydroxide solution and concentrating; fine needles; air-dried; yield 2.5 g. or 83%, containing 28.6% of combined water. One recrystallization from water gave the pure compound.

Anal. Calcd. for $C_4H_6O_6Ca$: Ca, 21.08. Found (dried at 115° *in vacuo*): Ca, 21.09, 21.11.

S-Benzylthiuronium glycolate was prepared from 5 ml. of the glycolic acid solution; after neutralization with 5 N sodium hydroxide and evaporation nearly to dryness, a solution of the sodium glycolate in 3–4 ml. of hot water was added to a hot solution of 2.18 g. of S-benzylthiuronium chloride in 14 ml. of 95% ethanol. The product, isolated according to Donleavy,[16] was purified by recrystallization from 95% ethanol; m. p. 143° (corr.) alone or mixed with the salt prepared from authentic glycolic acid. *p*-Bromophenacyl glycolate, prepared from 8.5 ml. of the glycolic acid solution by the usual procedure[17] and recrystallized several times from aqueous ethanol, melted at 142° (corr.) and showed no depression when mixed with the ester from authentic glycolic acid.

Anal. Calcd. for $C_{10}H_9O_4Br$: Br, 29.3. Found: Br, 29.6.

Oxidation of Alpha-Methyl-*d*-arabinofuranoside.[18]—The furanoside (1.8300 g.), dried to constant weight in an evacuated desiccator over phosphorus pentoxide, was made up to 25 ml. of solution in water at 20°; its specific rotation was +120.5°, the solution rotating 17.64° to the right in a 2-dm. tube. Exactly 24 ml., containing 1.7568 g. of the furanoside, was added to 25 ml. of 0.5365 M periodic acid solution (1.25 molecular equivalents) in a 50-ml. volumetric flask; the solution, made up to 50 ml. at 20° with water and kept in a 20° room, showed $[M]_D \times 10^{-2}$: +196.9 (five minutes); +194.8 (twenty minutes); +193.5 (thirty-five minutes); +191.2 (eighty minutes); +189.2 (three hours); +188.4 (five hours); +186.4, constant (twenty-four hours). After twenty-three hours an analysis of 5 ml. of the solution showed 12.6% excess periodic acid, or the reaction of 1.09 molecular equivalents.[19]

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[15] L′-methoxy-diglycolic acid, because of its acetal structure, should be expected to undergo hydrolysis readily; apparently the acetal is hydrolyzed nearly completely during the heating and the subsequent bromine oxidation by which hydrobromic acid is generated. It is noteworthy that the parent methyl-aldopentopyranoside is much more resistant to acid hydrolysis than the derived acetal; the cleavage of the carbon chain of the pyranoside ring increases the ease of hydrolysis.

[16] Donleavy, THIS JOURNAL, **58**, 1004 (1936).

[17] Judefind and Reid, *ibid.*, **42**, 1043 (1920); Hann, Reid and Jamieson, *ibid.*, **52**, 819 (1930).

[18] Supplied by Miss Edna Montgomery. The properties of the furanoside, particularly pertinent being its hygroscopicity, are described by Montgomery and Hudson.[5]

[19] From the difficulty experienced in obtaining sufficiently large samples of the furanoside in the anhydrous condition, it seems probable that the discrepancy between the rotation of +120.5° of the sample oxidized and the value +123° assigned to the pure compound[5] is due to moisture. Calculated on this assumption the sample (1.7210 g.) reacted with 1.12 molecular equivalents of periodic acid and the final $[M]_D \times 10^{-2}$ was +190.2 (twenty-four hours) corresponding to a specific rotation of +117.3° for the dialdehyde. The reaction of the excess of one molecular equivalent of periodic acid

TABLE V

ROTATORY CHANGES DURING THE OXIDATION OF THE METHYL HEXOSIDES TO DIALDEHYDES[a]

2.4296 g. of anhydrous methyl hexoside or the equivalent as hydrate[20] and 98 ml.[b] of 0.2689 *M* HIO_4 solution[c]

α-Methyl-*d*-galactoside		α-Methyl-*d*-glucoside		α-Methyl-*d*-guloside		α-Methyl-*d*-mannoside		β-Methyl-*d*-galactoside		β-Methyl-*d*-glucoside	
Time after soln., min.	$[M]_D \times 10^{-2}$	Time after soln., min.	$[M]_D \times 10^{-2}$	Time after soln., min.	$[M]_D \times 10^{-2}$	Time after soln., min.	$[M]_D \times 10^{-2}$	Time after soln., min.	$[M]_D \times 10^{-2}$	Time after soln., min.	$[M]_D \times 10^{-2}$
0	+380.7[d]	0	+308.4[d]	0	+232.1[d]	0	+153.3[d]	0	+ 1.4[d]	0	− 66.4[d]
2.9	+291.5	6.5	+256.0	3.5	+231.0	9	+199.9	8	−212.6	3.1	− 97.9
4.2	+260.1	10	+239.8	8.4	+229.3	14	+202.9	10	−217.4	7.3	−126.0
5.2	+240.9	13	+230.4	22.1	+221.7	20	+204.4	14.5	−224.9	11	−142.2
7.6	+212.1	16	+223.4	34	+217.8	33	+204.3	20.3	−228.6	16.6	−162.5
10.1	+198.5	20.5	+216.8	49.9	+214.6	51	+202.7	37.3	−233.3	31.6	−182.8
14	+189.5	26.5	+211.1	60	+212.7	80	+201.1	63	−237.0	50.2	−197.8
18	+186.2	37.5	+206.9	87	+207.2	110	+198.8	103	−238.0	77.8	−209.8
28	+187.6	66.5	+203.3	120	+202.3	145	+197.4	190	−239.3	111.4	−218.5
46	+190.5	120	+200.1	198	+198.5	180	+196.1	280	−240.0	175.3	−227.2
77	+193.1	218	+197.8	265	+197.1	265	+194.6	458	−240.0	230	−230.7
132	+194.5	293	+197.0	24 hrs.	+195.3	420	+193.7			298	−234.4
174	+195.0	413	+196.2							25 hrs.	−244.1
269	+195.7										
374	+195.7										

[a] See Fig. 1. [b] The volume of the solution, measured at 20° after completion of the reaction, was practically 100 ml. [c] The solutions were prepared at 20° and kept thereafter in a 20° room, but the temperature was variable due to the heat evolved in each of the oxidation reactions, the increase being 10° for α-methyl-*d*-galactoside. [d] Calcd. from the usually accepted specific rotations in water of the methyl-hexosides which are in the order listed: +196.1, +158.9, +109.4, +79, +0.7, −34.2. The value for α-methyl-guloside refers to its monohydrate.

Strontium D′-methoxy-D-hydroxymethyl-diglycolate in a yield of about 60% was prepared from the oxidation solution by the general directions given under the methyl-pentopyranosides. Recrystallized twice as fine needles from fifteen parts of water to which 10–15% of ethanol was added, and dried to constant weight at 105° *in vacuo* the anhydrous salt showed a specific rotation of −53.3° in water (*c*, 0.6).

Anal. Calcd. for $C_6H_8O_7Sr$: C, 25.74; H, 2.88; OCH_3, 11.1; Sr, 31.33. Found: C, 25.74, 25.80; H, 3.16, 3.12; OCH_3, 11.0, 10.9; Sr, 31.29, 31.36.

The identification of the strontium salt as a derivative of D′-methoxy-D-hydroxymethyl-diglycolic acid is confirmed by the specific rotation +26.1° (*c*, 1.4) of the dibasic acid obtained by liberating it from its pure strontium salt with an equivalent of hydrochloric acid (*cf.* Table I).

Oxidation of the Methyl-hexosides.—The procedure was the same as described for the methyl-pentopyranosides, using 98 ml. of 0.2689 *M* periodic acid solution and 2.4296 g. of pure anhydrous methyl-hexoside,[20] or a multiple of these quantities. The rotatory changes are shown in Table V; the results of analyses for periodic acid, carried out with 5 ml. of the solutions at specified times, are recorded in Table VI and show for each methyl-hexoside about the excess (5%) over two molecular equivalents added at the start. After completion of the oxidation reaction the solution from each alpha-methyl-hexoside was neutralized with strontium hydroxide solution and treated as outlined for the methyl-pentopyranosides. In Table VI is recorded the rotation of the sirupy D′-methoxy-D-hydroxymethyl-diglycolic aldehyde, isolated from each alpha-methyl-hexoside, and also the rotation after oxidation with bromine water in the presence of strontium carbonate. The yield of the crystalline hydrate of strontium D′-methoxy-D-hydroxymethyl-diglycolate, dried at 25° *in vacuo* over calcium chloride, was 65–70% from each alpha-methyl-hexoside; at this stage it usually showed a specific rotation in water of about −47° (*c*, 0.7). The strontium salt was recrystallized from fifteen parts of water, to which 10–15% ethanol was added, until the rotation of the anhydrous salt was constant. It crystallizes readily as fine needles which, after being dried in an evacuated desiccator over calcium chloride, contain two moles of combined water. Calcd. for $C_6H_8O_7Sr{\cdot}2H_2O$: H_2O, 11.41. Found H_2O (dried at 105° *in vacuo*): 11.66. The identity of the strontium salt from the four alpha-

TABLE VI

CONSUMPTION OF PERIODIC ACID. ROTATIONS BEFORE AND AFTER BROMINE OXIDATION OF THE DIALDEHYDES

Methyl hexoside	HIO_4 Analysis Time, hrs.	HIO_4 Analysis Excess, %	Rotation[a] of sirupy dialdehyde α_D	Rotation[b] after bromine oxidation α_D
α-Methyl-*d*-galactoside	5	5.2	+2.00	−0.73
α-Methyl-*d*-glucoside	6	6.9	+1.99	− .68
α-Methyl-*d*-guloside	24	4.7	+1.98	− .69
α-Methyl-*d*-mannoside	6	6.1	+1.92	− .69
β-Methyl-*d*-galactoside	6	5.8	−2.25	+ .48
β-Methyl-*d*-glucoside	25	5.2	−2.24	+ .49[c]

[a] In aqueous solution (250 ml.); 2-dm. tube. [b] In aqueous solution (500 ml.); 2-dm. tube. [c] Barium L′-methoxy-D-hydroxymethyl-diglycolate.

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could be caused by slight hydrolysis of the glycoside during the oxidation reaction, or a slight contamination of the sample by a pyranoside form.

[20] In the case of alpha-methyl-*d*-guloside its crystalline monohydrate (2.6552 g.), and of beta-methyl-*d*-glucoside its hemihydrate (2.5425 g.), was used. The carefully purified alpha-methyl-*d*-guloside monohydrate melted at 76–77° and showed a specific rotation of +109.4° in water (*c*, 2.2) in agreement with the values of Isbell [*J. Research Nat. Bur. Standards*, **8**, 6 (1932)].

TABLE VII

ROTATIONS AND ANALYSES OF STRONTIUM D′-METHOXY-D-HYDROXYMETHYL-DIGLYCOLATE FROM THE ALPHA-METHYL-HEXOSIDES

Methyl-hexoside	$[\alpha]^{20}_{D}$ in water[b]	$C_6H_8O_7Sr$[a] Found, % C	H	OCH_3	Sr	
Calculated values		25.74	2.88	11.1	31.33	
α-Methyl-*d*-galactoside	−53.5°				31.25	
α-Methyl-*d*-glucoside	−52.9°				31.25	31.17
α-Methyl-*d*-guloside	−52.7°	25.71	2.86	10.9	31.23	31.16
		25.80	3.12	10.9		
α-Methyl-*d*-mannoside	−53.0°				31.27	31.13

[a] Dried to constant weight at 105° *in vacuo*. The anhydrous salt is quite hygroscopic. [b] C = 0.58–0.65 g. per 100 ml. of solution. At concentrations of 0.6–1.2 g. per 100 ml. the rotation, which varies with the concentration, may be expressed by the equation: $[\alpha]^{20}\mathrm{D} = -48.6° - 7.36\ C$.

methyl-hexosides is shown by the rotations and analyses given in Table VII. A confirmation of this identification is afforded by the agreeing values of the specific rotation of D′-methoxy-D-hydroxymethyl-diglycolic acid, obtained by liberating it with an equivalent of hydrochloric acid from the pure strontium salt derived from each of the four alpha-methyl-hexosides (*cf.* Table I).

Barium L′-Methoxy-D-hydroxymethyl-diglycolate from Beta-methyl-*d*-glucoside.—The strontium salt prepared from beta-methyl-*d*-galactoside by the usual procedure unfortunately was not crystalline. The galactoside as shown by the data in Tables V and VI utilizes two moles of periodic acid in the manner typical of the hexopyranoside structure and yields a dialdehyde rotating about the same as that from beta-methyl-*d*-glucoside. This amorphous strontium salt appeared therefore to be the normal product from the beta-methyl-*d*-aldohexopyranosides, but its amorphous nature caused us to change to the barium salt, which crystallized quite readily when prepared from beta-methyl-*d*-glucoside.

After completion of the oxidation of beta-methyl-*d*-glucoside, the solution was neutralized with barium hydroxide solution and the procedure for the methyl-pentopyranosides was followed with the substitution of barium carbonate for strontium carbonate. The yield of crystalline barium salt, dried in an evacuated desiccator over calcium chloride and showing a specific rotation of +34 to +35° in water (c, 1.5), was 15 g. from 12.2 g. of beta-methyl-*d*-glucoside hemihydrate. Recrystallized twice from water as fine needles of the dihydrate (air-dried), the barium salt after being dried at 100° *in vacuo* showed the specific rotation[21] +35.9° in water (c, 3.4) which was unchanged by another recrystallization. The anhydrous salt is quite hygroscopic.

Anal. Calcd. for $C_6H_8O_7Ba{\cdot}2H_2O$: H_2O, 9.86. Found (dried at 100° *in vacuo*): H_2O, 9.92, 9.97. Calcd. for $C_6H_8O_7Ba$: C, 21.86; H, 2.45; OCH_3, 9.4; Ba, 41.70. Found: C, 21.84, 21.91; H, 2.58, 2.67; OCH_3, 9.3, 9.2; Ba, 41.72, 41.66.

The rotation of L′-methoxy-D-hydroxymethyl-diglycolic acid in water, from the barium salt and an equivalent of hydrochloric acid, is recorded in Table I.

Proof of Structure of the Strontium and Barium Salts from the Methyl-hexosides.—D′-Methoxy-D-hydroxymethyl-diglycolic acid, prepared from 15 g. of pure hydrated strontium salt,[22] was hydrolyzed in aqueous solution; the hydrolyzed acid was oxidized with bromine water and neutralized with barium hydroxide solution, all as described for the structure of strontium L′-methoxy-diglycolate. From the barium oxalate (5.7 g.) was prepared oxalic acid dihydrate of m. p. 99.5–101° which, after dehydration at 100°, melted at 189–190°; it was characterized further by the previously mentioned analyses.

The filtrate from the barium oxalate, freed from barium with sulfuric acid, from bromine ions with silver carbonate and from excess silver with hydrogen sulfide, was concentrated *in vacuo* to about 200 ml., filtered and neutralized to phenolphthalein with pure calcium hydroxide solution. The solution was concentrated *in vacuo* to a sirup which crystallized readily, yielding about 6 g. of crude calcium *d*-glycerate. After two recrystallizations from water and drying in the air, the calcium *d*-glycerate dihydrate melted at 141–142° (uncorr.) and showed a specific rotation in water of +14.6 ± 0.5° compared with m. p. 138° and specific rotation +14.07° found by Anderson.[23]

After the exact removal of the barium with sulfuric acid from 250 ml. of an aqueous solution containing 19.4 g. of pure anhydrous barium salt (barium L′-methoxy-D-hydroxymethyl-diglycolate) prepared from beta-methyl-*d*-glucoside, the solution was concentrated *in vacuo* to 200 ml., the organic acid was hydrolyzed by heating and treated thereafter by the above procedure for the preparation of barium oxalate (6.9 g.) and calcium *d*-glycerate (8.5 g. of crude). The oxalic acid dihydrate from the barium oxalate melted at 99.5–101°, and was characterized further as previously described. The calcium *d*-glycerate dihydrate after three recrystallizations from water showed m. p. 141–142° (uncorr.) and specific rotation +14.9 ± 0.5° in water.

Anal. Calcd. for $C_6H_{10}O_8Ca{\cdot}2H_2O$: H_2O, 12.59; Ca, 14.00. Found (from the strontium salt): H_2O, 12.78; Ca, 13.95, 13.78; (from the barium salt) H_2O, 12.61; Ca, 13.91, 13.86.

We express our thanks to Dr. R. M. Hann for a supply of galactose and S-benzylthiuronium

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[21] Variation of the rotation with the concentration should be anticipated from the close relationship to the strontium salts.

[22] The sample of strontium salt was prepared by the oxidation of alpha-methyl-*d*-mannoside with barium hypobromite.

[23] Anderson, *Am. Chem. J.*, **42**, 421 (1909); *cf.* Nef, Hedenburg and Glattfeld, THIS JOURNAL, **39**, 1650 (1917); Fischer and Jacobs, *Ber.*, **40**, 1069 (1907).

chloride, to Dr. Alice T. Merrill for the methylguloside, to Miss Edna M. Montgomery for the methyl-arabinosides and to Mr. C. G. Remsburg for carrying out some of the analyses.

Summary

The oxidation of alpha-methyl-*d*-mannopyranoside with barium hypobromite was shown[2] to produce a dibasic acid which was isolated as its crystalline strontium salt and was proved to be a derivative of diglycolic acid (D′-methoxy-D-hydroxymethyl-diglycolic acid). The same strontium salt has been prepared in yields of 65–70% through oxidation of four alpha-methyl-hexosides (alpha-methyl-*d*-mannoside, *d*-glucoside, *d*-galactoside and *d*-guloside) with periodic acid followed by oxidation of the resulting dialdehyde with bromine water kept neutral with strontium carbonate. The structure of the strontium salt, particularly the presence of the *d*-glyceric acid moiety in its molecule, proves each of the four alpha-methyl-hexosides to be of the pyranoside type, this being the first proof for alpha-methyl-*d*-guloside. Beta-methyl-*d*-glucoside produces by way of these oxidation reactions a crystalline barium salt which also has the *d*-glyceric acid grouping in its molecule; evidence is presented that this salt is barium L′-methoxy-D-hydroxymethyl-diglycolate from which follows the pyranoside structure for beta-methyl-*d*-glucoside.

The alpha forms of methyl-*d*-arabinoside (−17°) and methyl-*d*-xyloside (+154°) yield another crystalline strontium salt (strontium D′-methoxy-diglycolate) and the beta forms of these two glycosides −245 and −65°, respectively) produce strontium L′-methoxy-diglycolate, the optical antipode of the salt from the alpha forms. Since the latter two strontium salts contains the glycolic acid structure in their molecules the four parent methyl-pentosides must have the pyranoside structure. A third crystalline methyl-*d*-arabinoside (+123°) yields the strontium salt with the *d*-glyceric acid grouping (the one from the alpha-methyl-*d*-aldohexopyranosides); this new methyl-arabinoside must therefore possess the furanoside structure and the alpha configuration.

The cleavage type of oxidation, having wide application among the glycosides, thus provides a new method for the determination of ring structures and for the correlation of the configuration of carbon atom 1 of glycosides. It also affords the most direct way of correlating the configuration of the sugars with glyceric acid.

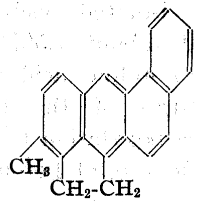
WASHINGTON, D. C. RECEIVED APRIL 5, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of 1,2-Benzanthracene Derivatives Related to 3,4-Benzpyrene

BY MELVIN S. NEWMAN

In seeking to account for the carcinogenic activity of methylcholanthrene, I, and cholanthrene, II, in terms of chemical constitution,[1] Fieser and the author[2] prepared 5,10-dimethyl-1,2-benzanthracene, III, and 10-methyl-1,2-benzanthracene, IV. In that publication it was reported that III is comparable in rapidity of action to I and II. The results of further biological tests[3] indicate that IV has approximately the same activity as I, II and III. Thus, in viewing the structures of these four compounds, the conclusion is to be drawn that the structural feature necessary for strongly developed cancer-producing properties in hydrocarbons of the 1,2-benzanthracene series is substitution at position 10.



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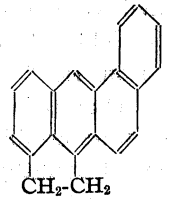
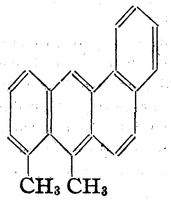


II



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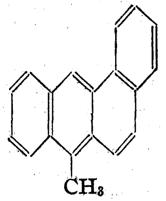

IV

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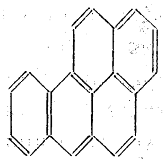
(1) For a more complete discussion of the carcinogenic activity of 1,2-benzanthracene derivatives see Fieser, *et al.*, *Am. J. Cancer*, **29**, 260 (1937).

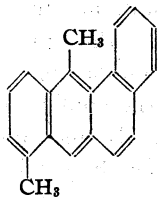
(2) Fieser and Newman, THIS JOURNAL, **58**, 2376 (1936).

(3) Private communication from Dr. M. J. Shear. See also Fieser and Hershberg, *ibid.*, **59**, 394 (1937).

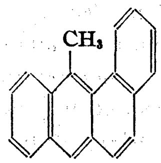
Since position 10 is a meso position, the question arises as to what effect substitution at the other meso position 9 would have. In this connection it is interesting to note that 3,4-benzpyrene, V,[4] the only known actively carcinogenic hydrocarbon which is not a 10-substituted 1,2-benzanthracene, may be considered as a 9-substituted derivative. Furthermore, 8,9-dimethylene-1,2-benzanthracene,[5] an isomer of II, is carcinogenic although its action is slow.[6]


V

In order to obtain further information concerning the effect of substitution at position 9, the preparation of 5,9-dimethyl-1,2-benzanthracene, VI, and 9-methyl-1,2-benzanthracene, VII, was undertaken. In this paper the synthesis of these two hydrocarbons is reported.[7]



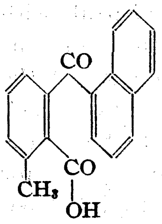
VI



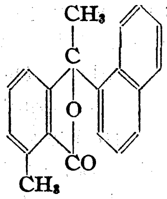
VII

From the reaction of 1-naphthylmagnesium bromide with 3-methylphthalic anhydride, prepared by sulfur dehydrogenation of the addition product from piperylene and maleic anhydride[8] a mixture was obtained from which the desired keto acid, VIII, was isolated easily in 52% yield. A small amount (about 1.5%) of the isomeric 2-(1-naphthoyl)-*m*-toluic acid was also separated. The structures of the keto acids were established by decarboxylation to the known 1-naphthyl *m*-tolyl and *o*-tolyl ketones.[9] This ratio of isomers produced from 3-methylphthalic anhydride in the Grignard reaction stands in marked contrast to the ratio of isomers formed in the Friedel–Crafts condensation. Hayashi, *et al.*,[10] condensed 3-methylphthalic anhydride with benzene and obtained approximately 38% of 2-benzoyl-*m*-toluic acid and 10% of 6-benzoyl-*o*-toluic acid.

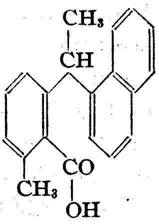
On treatment with an excess of methylmagnesium bromide, VIII was converted into the lactone, IX, in 74% yield. This lactone was reduced by zinc amalgam and hydrochloric acid in acetic acid to the acid, X, and, on cyclization with concentrated sulfuric acid at room temperature followed by reduction of the crude anthrone with zinc dust and alkali, the hydrocarbon, VI, was obtained.



VIII



IX



X

By repeating the above series of reactions using phthalic anhydride in place of 3-methylphthalic anhydride, the hydrocarbon, VII, was prepared. Of interest are the poor yields obtained in the two-step conversions of X and 2-(1-naphthylethyl)-benzoic acid into VI and VII, respectively, in contrast to the good yields in the somewhat similar preparation of III and IV.[2]

Experimental[11]

Preparation of 3-Methylphthalic Anhydride.—From the reaction between maleic anhydride and piperylene[12] was obtained 3-methyl-1,2,3,6-tetrahydrophthalic anhydride,[8] m. p. 61–62°, b. p. 155–156° at 12 mm. The observations of Farmer and Warren concerning the drop in yield of addition product when the reaction was carried out without cooling were confirmed. On dehydrogenation of 52 g. of addition product by heating at 250–260° for two hours with 20 g. (1 mol) of sulfur there was obtained, after

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(4) Cook, Hewett and Hieger, *J. Chem. Soc.*, 395 (1933).

(5) Fieser and Seligman, THIS JOURNAL, **57**, 2174 (1935).

(6) Shear, *Am. J. Cancer*, **28**, 334 (1936).

(7) The new hydrocarbons are being tested for carcinogenic activity by Dr. M. J. Shear. After approximately three and one-half months, 5,9-dimethyl-1,2-benzanthracene, VI, has produced tumors in 18 of 20 mice and appears to rank with I in rapidity of production of tumors. During the same period, 9-methyl-1,2-benzanthracene, VII, has only produced one tumor in 20 mice. While in press the synthesis of VII by Cook, *et al.*, *J. Chem. Soc.*, 393 (1937), has been reported.

(8) Diels and Alder, *Ann.*, **470**, 102 (1929); Farmer and Warren, *J. Chem. Soc.*, 3221 (1931).

(9) Fieser and Martin, THIS JOURNAL, **58**, 1443 (1936); Bachmann, *J. Org. Chem.*, **1**, 347 (1936). Bachmann reports a melting point of 59–61° for 1-naphthyl *o*-tolyl ketone whereas Fieser and Martin, *loc. cit.*, Fieser and Newman, ref. 2, and the author give 51.5–52.5°. To clear up this discrepancy the author synthesized this ketone by Bachmann's method. The product melted at 59–61° but on crystallization of a small amount from methanol another form (thin plates) crystallized having a melting point of 51.5–52.5°. On standing for several months this sample had a melting range of 53–57°.

(10) Hayashi, Tsuruoka, Morikawa and Namikawa, *Bull. Chem. Soc. Japan*, **11**, 184 (1936).

(11) All melting points are corrected. Analyses (semi-micro) by Mrs. G. M. Wellwood, Converse Memorial Laboratory, Harvard University.

(12) The author is indebted to Drs. Dolliver, Gresham and Kistiakowsky of Harvard University for the piperylene.

vacuum distillation and crystallization from benzene–ligroin, 28 g. (54%) of sulfur-free 3-methylphthalic anhydride, m. p. 115–116°.

Synthesis of 5,9-Dimethyl-1,2-benzanthracene

6-(1-Naphthoyl)-*o*-toluic Acid, VIII.—The filtered Grignard reagent prepared from 23 g. of 1-bromonaphthalene and an excess of magnesium in 120 cc. of ether and 15 cc. of benzene[13] was added rapidly (during thirty seconds) to a well-stirred solution of 16.2 g. of 3-methylphthalic anhydride in 125 cc. of benzene. No attempt was made to condense the ether which boils off during this vigorous reaction as experience showed that when this was done, the increase in pressure was sufficient to cause mercury to splash out of the mercury-sealed stirrer. The reaction mixture was worked up as before[2] and the crude keto acids (17.8 g.) recrystallized from 65 cc. of glacial acetic acid, yielded 15.2 g. (52%) of VIII, m. p. 164–165.5°. For analysis a portion was recrystallized twice from acetic acid, the melting point rising to 165.6–166.8°.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.86. Found: C, 78.44; H, 4.85.

From the original mother liquors on concentration, slow crystallization, separation of crystals by hand, and recrystallization from acetic acid, was obtained 0.45 g. (1.5%) of the isomeric 2-(1-naphthoyl)-*o*-toluic acid as fine white needles, m. p. 234–235° after sintering at 230°.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.86. Found: C, 78.23; H, 5.25.

Decarboxylation of the Acids.—These reactions were carried out as before:[2] from VIII was obtained 1-naphthyl *m*-tolyl ketone, m. p. and mixed m. p. 74.5–75.8°;[9] and from 2-(1-naphthoyl)-*m*-toluic acid was obtained 1-naphthyl *o*-tolyl ketone, m. p. and mixed m. p. 51.5–52.5°.[9]

Lactone of 6-(α-Hydroxy-α-1-naphthylethyl)-*o*-toluic Acid, IX.—The filtered Grignard reagent from 1.8 g. of magnesium and methyl bromide in 90 cc. of ether was added slowly to a warm well-stirred solution of 8.7 g. of VIII in 250 cc. of benzene. The initial cream colored complex turned greenish-yellow and finally light yellow. After two hours of refluxing the mixture was decomposed with dilute hydrochloric acid. From the neutral fraction, freed of acids by a sodium carbonate washing, was obtained 6.4 g. (74%) of lactone, IX, m. p. 131.4–132.0° as white plates. A portion was recrystallized from alcohol, m. p. 131.6–132.0°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.30; H, 5.66. Found: C, 83.07; H, 5.67.

6-(α-1-Naphthylethyl)-*o*-toluic Acid, X.—A solution of 4.74 g. of IX in 100 cc. of acetic acid was refluxed over zinc amalgam[14] for ten hours with gradual addition of 100 cc. of concentrated hydrochloric acid. The acid fraction yielded 1.9 g. (40%) of X as colorless needles, m. p. 156.0–158.5° from benzene. A portion twice crystallized from acetic acid had a melting point of 162–162.6°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.72; H, 6.25. Found: C, 82.77; H, 6.09.

5,9-Dimethyl-1,2-benzanthracene, VI.—To 20 cc. of concentrated sulfuric acid at 20° was added 1.54 g. of powdered X with swirling until a homogeneous orange solution resulted. After two hours the acid was poured on ice and the pale yellow anthrone collected by filtration. It was immediately transferred to a flask with 2 g. of zinc dust, previously activated with copper sulfate, and 100 cc. of 15% sodium hydroxide. The mixture was refluxed for five hours, a few drops of amyl alcohol being added to prevent excessive foaming. After strongly acidifying with hydrochloric acid, the product, VI, was collected on a filter and crystallized from benzene–alcohol to yield 0.50 g. of white shiny plates, m. p. 135–135.5°. In ultraviolet light the hydrocarbon has a brilliant blue fluorescence.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.51; H, 6.57.

Synthesis of 9-Methyl-1,2-benzanthracene

Lactone of 2-(α-Hydroxy-α-1-naphthylethyl)-benzoic Acid.—The filtered Grignard reagent from 7.29 g. of magnesium and methyl bromide in 200 cc. of ether was added slowly to a warm well-stirred solution of 13.80 g. of *o*-(1-naphthoyl)-benzoic acid[15] in 200 cc. of ether and 250 cc. of benzene. The pale yellow complex which immediately separated gradually took on a greenish tinge and finally dissolved to give a pale yellow solution. After two hours of refluxing the mixture was decomposed with dilute hydrochloric acid. From the neutral fraction, freed of acids by washing with sodium carbonate, was obtained 8.0 g. (58%) of almost colorless plates, m. p. 152.8–153.6°. A sample of this compound, the desired lactone, recrystallized from alcohol melted at 154.5–155.0°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.18; H, 5.15. Found: C, 83.35; H, 5.33.

***o*-(α-1-Naphthylethyl)benzoic Acid.**—A solution of 8.6 g. of the above lactone in 150 cc. of acetic acid was refluxed over 50 g. of zinc amalgam for twelve hours with slow addition of 150 cc. of concentrated hydrochloric acid in 50 cc. of acetic acid. The mixture was diluted with water and thoroughly extracted with ether. The acid reduction product was separated by means of extraction with sodium carbonate and on crystallization from benzene–ligroin, 7.1 g. (82%) of the desired acid was obtained as white needles, m. p. 168–169°. A sample recrystallized from acetic acid melted at 169.4–170°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.49; H, 5.89.

9-Methyl-1,2-benzanthracene.—For cyclization, 1.94 g. of the above acid was powdered and added to a cold solution of 1 g. of boric acid in 20 cc. of concentrated sulfuric acid. After two hours at room temperature the orange solution was poured on ice and the crude pale yellow anthrone reduced by boiling for six hours with 2 g. of zinc dust (activated) and 100 cc. of 12% sodium hydroxide. Amyl alcohol was again necessary to prevent foaming. After working the reaction mixture up as above there was obtained 0.45 g. (26%) of pale yellow flat needles, m. p.

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[13] All benzene used in this and other Grignard reactions was thiophene free.

[14] The poor yield in this step which ordinarily (reference 2 and in this paper below) proceeds in excellent yield was probably due in this case to the poor quality of the zinc used. During the reduction the surface of the zinc had an entirely different appearance from the usual bright surface in such reactions.

[15] Weizmann, Bergmann and Bergmann, *J. Chem. Soc.*, 1367 (1935); Groggins and Newton, *Ind. Eng. Chem.*, **22**, 157 (1930).

138.4–138.8°. Neither the color nor the melting point was improved by chromatographic adsorption using activated alumina.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.83. Found: C, 94.20; H, 5.93.

Summary

A rather general method is described for the synthesis of 1,2-benzanthracenes containing a substituent at the meso position 9. This method involves the following steps: reaction of 1-naphthylmagnesium bromide with phthalic anhydride (or 3-methylphthalic anhydride); addition of methylmagnesium bromide to the ketonic carbonyl group of the resulting keto acid; reduction of the resulting lactone to an acid; and cyclization and reduction to the hydrocarbon. In this manner, 5,9-dimethyl-1,2-benzanthracene and 9-methyl-1,2-benzanthracene have been prepared for the purpose of comparing their possible carcinogenic activity with that of 10-methyl-1,2-benzanthracene and that of 3,4-benzpyrene.

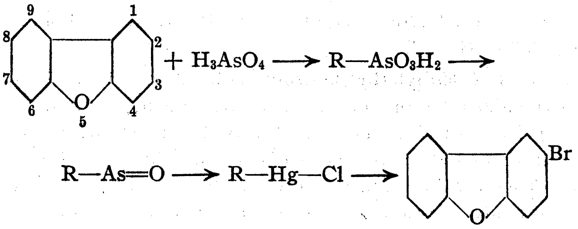
COLUMBUS, OHIO RECEIVED APRIL 3, 1937

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

Arsenicals Containing the Dibenzofuran Nucleus

BY BENJAMIN F. SKILES[1] AND CLIFF S. HAMILTON

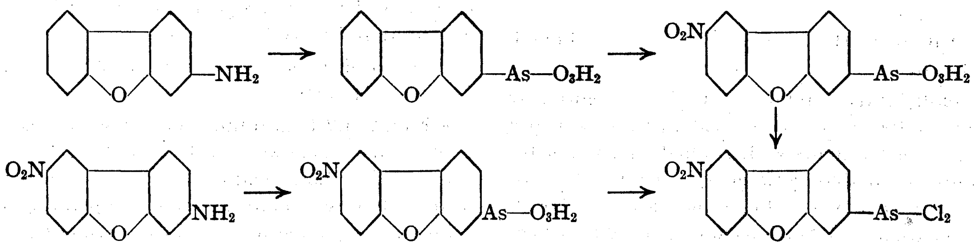
Dibenzofuran was arsonated directly by heating it with arsenic acid. The structure of the arsonic acid formed was problematical for, in the case of dibenzofuran, the nature of the entering groups has a marked effect upon the position assumed by nuclear substituents. Nitration involves principally the 3-position;[2] sulfonation,[3] and halogenation[4] favor the 2-position exclusively, while in metalation[5] the substituent enters the 4-position. The following sequence of reactions



was used to prove that dibenzofuran on direct arsonation yields 2-dibenzofurylarsonic acid.[3,6]

3-Dibenzofurylarsonic acid[7] was prepared by means of a Bart[8] reaction utilizing 3-aminodibenzofuran as a starting material. The product was nitrated to yield nitro-3-dibenzofurylarsonic acid, and then converted into nitro-3-dibenzofuryldichloroarsine which on heating to 350° with mercuric acetate gave 2-nitrodibenzofuran. This indicated that the nitro group entered either the 2- or the 8-position. Since the arsono group is a meta director in the benzene ring, and 3-nitrodibenzofuran on nitration yields 3,8-dinitrodibenzofuran, the latter structure seemed the more probable. The nitration product was shown to be 8-nitro-3-dibenzofurylarsonic acid by preparing a sample of this acid having a known structure and converting it into the dichloroarsine which was identical with the one prepared from the nitration product (mixed m. p.).

3-Dibenzofurylarsonic acid on sulfonation gave sulfo-3-dibenzofurylarsonic acid. The structure of this compound has not been established but it is probably 8-sulfo-3-dibenzofurylarsonic acid.



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(1) Parke, Davis and Company Fellow.

(2) Cullinane, *J. Chem. Soc.*, 2267 (1930).

(3) Gilman, Smith, and Oatfield, THIS JOURNAL, **56**, 1412 (1934).

(4) Mayer and Krieger, *Ber.*, **55**, 1659 (1922).

(5) Gilman and Young, THIS JOURNAL, **56**, 1415 (1934).

(6) Gilman has shown that replacement of the Hg–Cl group by bromine is reliable under the experimental conditions used in this reaction.

(7) Since the completion of this investigation, an article by Davies and Othen has appeared recording the preparation of dibenzofurylarsonic acids containing the arsono group in the 2-, 3- and 4-positions; *J. Chem. Soc.*, 1236 (1936).

(8) Bart, *Ann.*, **429**, 55 (1922).

Experimental

2-Dibenzofurylarsonic Acid.—An intimate mixture of 30 g. of arsenic acid and 30 g. of dibenzofuran was heated at 175° for three hours with constant stirring. The temperature was then increased to 220° for ten minutes, the mixture becoming very tarry. This mass was extracted first with water and then with *N* sodium hydroxide. The alkaline solution was made neutral to litmus with hydrochloric acid and the precipitated tar filtered off. Acidification of the filtrate to Congo red paper precipitated 2-dibenzofurylarsonic acid; purified by extraction with hot concentrated hydrochloric acid and crystallization from glacial acetic acid; yield 6 g., not melted at 250°.

Anal. Calcd. for $C_{12}H_9O_4As$: As, 25.68. Found: As, 25.52, 25.57.

2-Dibenzofurylarsine Oxide.—Five grams of 2-dibenzofurylarsonic acid was suspended in 50 cc. of boiling glacial acetic acid and 5 cc. of phosphorus trichloride, dissolved in 20 cc. of glacial acetic acid, was added slowly. The solution was refluxed for thirty minutes and then cooled in an ice-bath, the 2-dibenzofuryldichloroarsine separating as an oil which solidified on standing. This product was not isolated, but was hydrolyzed to the arsine oxide by refluxing with boiling water for two hours. The water-insoluble product was recrystallized from a methyl cellosolve–water mixture; yield 80%, not melted at 250°.

Anal. Calcd. for $C_{12}H_7O_2As$: As, 28.96. Found: 29.02, 29.00.

Structure Proof.—Two grams of 2-dibenzofurylarsine oxide and 5 g. of mercuric acetate were dissolved in 150 cc. of glacial acetic acid and refluxed for one hour. Addition of a glacial acetic acid solution of calcium chloride gave a white precipitate of 2-dibenzofurylmercuric chloride which was extracted with water and recrystallized with acetone; yield 80%, m. p. 235° (checks value in literature[3]).

Gilman's method[3] was used to convert the 2-dibenzofurylmercuric chloride to 2-bromodibenzofuran. The product obtained was identified by means of a mixed melting point with a known sample of 2-bromodibenzofuran prepared by brominating dibenzofuran.[4]

3-Dibenzofurylarsonic Acid.—Eighteen grams of 3-aminodibenzofuran was diazotized in 1.0 liter of *N* hydrochloric acid and the solution added slowly to a mechanically stirred mixture containing 19 g. of sodium arsenite, 0.25 g. of copper sulfate, and 300 g. of sodium carbonate dissolved in 8.0 liters of water and cracked ice. The resulting solution was stirred for four hours, allowed to stand at room temperature for twelve hours, and then filtered through a charcoal mat. Acidification of the filtrate with concd. hydrochloric acid precipitated the 3-dibenzofurylarsonic acid; yield 70%. Recrystallization from glacial acetic acid gave a white crystalline compound, not melted at 275°.

Anal. Calcd. for $C_{12}H_9O_4As$: As, 25.68. Found: As, 25.55, 25.58.

3-Dibenzofuryldichloroarsine.—An 85% yield of this compound was obtained by adding slowly a solution of 10 cc. of phosphorus trichloride, dissolved in 25 cc. of glacial acetic acid, to a boiling suspension of 3-dibenzofurylarsonic acid in 75 cc. of glacial acetic acid, and refluxing the resulting solution for thirty minutes. On cooling, the dichloroarsine crystallized out as a white solid; an additional amount was obtained by adding 10 cc. of concd. hydrochloric acid to the mother liquor; m. p. 130°, after recrystallization from glacial acetic acid.

Anal. Calcd. for $C_{12}H_7OAsCl_2$: As, 23.96; Cl, 22.68. Found: As, 24.00, 24.04; Cl, 22.44, 22.52.

3-Dibenzofurylarsine Oxide.—A theoretical yield of the oxide was obtained by boiling 3-dibenzofuryldichloroarsine for two hours with water. Recrystallization from a methyl cellosolve–water mixture gave a white solid, not melted at 250°.

Anal. Calcd. for $C_{12}H_7O_2As$: As, 28.96. Found: As, 29.03, 29.01.

8-Nitro-3-dibenzofurylarsonic Acid.—This compound was prepared by two different methods. In one, 8-nitro-3-aminodibenzofuran served as the starting compound, while in the other 3-dibenzofurylarsonic acid was used.

Method I.—Four grams of 8-nitro-3-aminodibenzofuran[9] dissolved in 120 cc. of glacial acetic acid was diazotized with 3 g. of sodium nitrite dissolved in 20 cc. of water. This solution was diluted with 200 cc. of aqueous 2 *N* hydrochloric acid and added slowly to a mechanically stirred solution containing 10 g. of sodium arsenite, 0.25 g. of copper sulfate, and 200 g. of sodium carbonate dissolved in 1.0 liter of water and cracked ice. The solution was stirred for three hours and after standing for twelve hours at room temperature was filtered through a charcoal mat. On acidification of the filtrate with hydrochloric acid 8-nitro-3-dibenzofurylarsonic acid separated; yield 35%; purified by extraction with glacial acetic and concd. hydrochloric acids followed by solution in alkali, filtration and precipitation with hydrochloric acid; yellow solid, not melted at 280°.

Anal. Calcd. for $C_{12}H_8O_6NAs$: As, 22.26. Found: As, 22.35, 22.37.

Method II.—Nine grams of 3-dibenzofurylarsonic acid was treated for two hours at 5° with fuming nitric acid (d. 1.48) and the resulting solution poured into 400 cc. of ice water. The arsonic acid separated as yellow solid; purified as above; yield 70%.

8-Nitro-3-dibenzofuryldichloroarsine.—Twenty grams of 8-nitro-3-dibenzofurylarsonic acid was suspended in 100 cc. of boiling glacial acetic acid and 20 cc. of phosphorus trichloride, dissolved in 30 cc. of glacial acetic acid, was added slowly. The solution was refluxed for thirty minutes and on cooling the dichloroarsine precipitated as a yellow solid. An additional amount was obtained by adding 125 cc. of concd. hydrochloric acid to the mother liquor. Recrystallization from glacial acetic acid gave an 80% yield; m. p. 152°.

Two preparations of 8-nitro-3-dibenzofuryldichloroarsine were made by this procedure. In one, the 8-nitro-3-dibenzofurylarsonic acid prepared from 8-nitro-3-aminodibenzofuran was used. In the other the product, obtained when 3-dibenzofurylarsonic acid was nitrated, served as the starting material. The dichloroarsines obtained from these two reactions were identical (mixed melting points).

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(9) Cullinane, *J. Chem. Soc.*, 2365 (1932).

Anal. Calcd. for $C_{12}H_6O_3NAsCl_2$: As, 20.95; Cl, 19.83. Found: As, 21.05, 21.04; Cl, 19.57, 19.61.

Structure Proof.—An intimate mixture of 15 g. of 8-nitro-3-dibenzofuryldichloroarsine and 15 g. of mercuric acetate was fused for ten minutes at 350°. An acetic acid extract of this melt on dilution with water gave 1 g. of a yellow solid, m. p. 149° after crystallization from an alcohol-acetone mixture. It was identified as 2-nitrodibenzofuran by means of a mixed melting point.[9] Reduction of this compound gave 2-aminodibenzofuran, m. p. 125°, and acetylation of the amine produced 2-acetaminodibenzofuran, m. p. 162°.

8-Nitro-3-dibenzofurylarsine Oxide.—A quantitative yield of the oxide was obtained by the hydrolysis of 2 g. of 8-nitro-3-dibenzofuryldichloroarsine with boiling water for four hours; light orange product after crystallization from methyl cellosolve, not melted at 250°.

Anal. Calcd. for $C_{12}H_6O_4NAs$: As, 24.75. Found: 24.67, 24.65.

8-Amino-3-dibenzofurylarsonic Acid.—A quantitative yield of this acid was obtained by reducing an alkaline solution of 8-nitro-3-dibenzofurylarsonic acid with hydrogen using the Raney catalyst.[10] Acidification to litmus with concd. hydrochloric acid produced a white precipitate of the amine which was recrystallized from dilute hydrochloric acid; not melted at 250°.

Anal. Calcd. for $C_{12}H_{10}O_4NAs$: As, 24.43. Found: As, 24.48, 24.44.

Sulfo-3-dibenzofurylarsonic Acid.—A suspension of 9 g. of 3-dibenzofurylarsonic acid in 60 cc. of concd. sulfuric acid was heated over a steam-bath for two hours. The solution was then cooled in an ice-bath and diluted with water until a heavy white precipitate was formed; not melted at 300° after recrystallization from water. The structure of this compound has not been proved but it is probably 8-sulfo-3-dibenzofurylarsonic acid.

Anal. Calcd. for $C_{12}H_9O_7SAs$: As, 20.16. Found: As, 20.30, 20.27.

Sulfo-3-dibenzofurylarsine Oxide.—An 80% yield of the oxide was obtained by bubbling sulfur dioxide through a solution of 0.5 g. of potassium iodide, and 1 g. of sulfo-3-dibenzofurylarsonic acid in 150 cc. of 2 *N* hydrochloric acid. At the end of twenty minutes the precipitated arsine oxide was filtered out and purified by salting it out of a water solution, not melted at 275°.

Anal. Calcd. for $C_{12}H_7O_6SAs$: As, 22.19. Found: As, 22.39, 22.37.

Summary

1. Direct arsonation of dibenzofuran gives 2-dibenzofurylarsonic acid as shown by structure proof; its oxide is described.

2. 3-Dibenzofurylarsonic acid has been prepared through the diazo reaction and converted into the dichloroarsine and oxide by reduction. Nitration of 3-dibenzofurylarsonic acid gives the 8-nitro derivative and from this the corresponding amine compound has been obtained by catalytic reduction.

3. 3-Dibenzofurylarsonic acid has been sulfonated directly.

LINCOLN, NEBRASKA RECEIVED MARCH 18, 1937

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(10) Raney, U. S. Patent 1,628,190 (1927).

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA, AND THE INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

Antioxidants and the Autoxidation of Fats. IX. The Antioxidant Properties of the Tocopherols

BY H. S. OLCOTT AND O. H. EMERSON

The unsaponifiable fraction of some vegetable oils exhibits marked antioxidant properties when small amounts are added to lard. Olcott and Mattill[1] have recorded some of the characteristics of the active principles which they called inhibitols. When wheat germ oil or cottonseed oil was used as the source, the inhibitol concentrates contained a large amount of vitamin E from which the inhibitols could not be separated. The successful isolation of three individual compounds possessing vitamin E activity from these oils by Evans, Emerson and Emerson[2-4] provided an opportunity for ascertaining the relationship between the inhibitols and tocopherols.

The three tocopherols and their allophanates were assayed for antioxidant activity by the oxygen absorption method previously described.[5] The tocopherols were effective antioxidants in lard and oleo oil, but had no activity in esters prepared from hydrogenated cottonseed oil (Table I). Since the inhibitol concentrates from wheat germ oil and cottonseed oil behave similarly,[6] it seems apparent that they owe at least part, and possibly all, of their antioxidant activity to the tocopherols. However, the inhibitols obtained

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(1) Olcott and Mattill, THIS JOURNAL, **58**, 1627 (1936).

(2) Evans, Emerson and Emerson, *J. Biol. Chem.*, **113**, 319 (1936).

(3) Emerson, Emerson and Evans, *Science*, **83**, 421 (1936).

(4) Emerson, Emerson, Mohammed and Evans, in press.

(5) French, Olcott and Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935).

(6) Olcott and Mattill, THIS JOURNAL, **58**, 2204 (1936).

from lettuce[7] and tomatoes[8] in the methanol fraction after distribution between petroleum ether and 92% methanol are presumably not tocopherols, since the latter, on distribution between these solvents, are found in the petroleum ether phase, and have, moreover, appreciably higher boiling points.

TABLE I

ANTIOXIDANT PROPERTIES OF THE TOCOPHEROLS AND THEIR ALLOPHANATES

Added antioxidant	% used	Induction period at 75°	
		Exptl.	Control
Substrate fat: Lard			
α-Tocopherol[a]	0.01	36	13
	.01	20	15
	.02	60	15
	.02	74	13
	.02	62	15
β-Tocopherol	.01	61	14
	.02	96	14
	.02	99	15
γ-Tocopherol[b]	.01	96	10
	.01	107	11
	.02	150	10
	.02	166	11
α-Tocopherol allophanate[c]	.02	85	20
	.02	114	17
β-Tocopherol allophanate[d]	.02	132	20
	.02	166	17
γ-Tocopherol allophanate[e]	.02	156	20
	.02	172	17
Oleo oil			
α-Tocopherol	.01	32	12
γ-Tocopherol	.01	110	12
	.02	360	12
Crude esters hydrogenated cottonseed oil			
α-Tocopherol	0.01	2.5	2.5
	.02	2.0	2.0

[a] Approximate minimum effective dose when administered to vitamin E deficient female rats; α-tocopherol, 1–3 mg.; β-tocopherol, 3–5 mg.; γ-tocopherol, 1–3 mg. Biological assays from the two laboratories showed reasonable agreement. [b] The γ-tocopherol and its allophanate used in these tests contained some α-tocopherol. [c] M. p. 157–158°. [d] M. p. 138°. [e] M. p. 135–135.5°.

The tocopherols are increasingly effective as antioxidants in the order α, β, γ. On the other hand, as vitamin E, β is less effective than α or γ. This lack of correlation between the antioxidant and vitamin properties of the pure substances offers an explanation for the previously observed lack of direct relationship in the concentrates.[1,6]

Vitamin E concentrates virtually free from antioxidant activity have been described.[7,8] A possible explanation of these results may be based on the assumption that the preparations were not completely hydrolyzed. Simple esters of the tocopherols are effective as the vitamin, but ineffective as antioxidants. The possibility that vitamin E may occur in nature in the form of an ester has been suggested previously.[9]

The antioxidant activity of the tocopherol allophanates (Table I) was unexpected, inasmuch as previous observations had indicated that the activity of inhibitols and of antioxidants of known structure depended on the presence of a free hydroxyl group.[1,10] However, the fact that α-naphthol allophanate[11] is also an effective antioxidant while cholesterol allophanate is not, suggests that the activity of the allophanates parallels that of the parent compounds.

Since antioxidants of known structure are phenolic in nature,[10] the antioxygenic activity of the tocopherols suggests that they may belong to this class of substances. The absorption spectrum of the tocopherols resembles that of hydroquinone; however, the tocopherols differ from most phenols in having little or no acidic properties.

Acknowledgment.—One of us (H. S. O.) is indebted to Lever Brothers Company for a grant in support of this work.

Summary

α, β and γ tocopherols and their allophanates are effective antioxidants in lard. The degree of protection afforded by the tocopherols is not proportional to their vitamin E activity.

IOWA CITY, IOWA
BERKELEY, CALIF.
RECEIVED APRIL 7, 1937

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[7] Olcott and Mattill, *J. Biol. Chem.*, **93**, 59, 65 (1931).

[8] Bradway and Mattill, THIS JOURNAL, **56**, 2405 (1934).

[9] Olcott, *J. Biol. Chem.*, **110**, 695 (1935).

[10] Olcott, THIS JOURNAL, **56**, 2492 (1934).

[11] The preparation and properties of this compound will be described in another place.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Condensation of Acetic Acid and Cyclohexene in the Presence of Boron Fluoride

BY H. L. WUNDERLY AND F. J. SOWA

The purpose of this study was to determine the effect of boron fluoride upon the formation of cyclohexyl acetate from cyclohexene and acetic acid.[1] A series of reactions was carried out at constant temperature with a variation in the percentage of boron fluoride and the time of reaction.

Experimental Part

The experimental procedure for all reactions was the same as that described below. The boron fluoride was used in the form of the acetic acid–boron fluoride compound which was prepared according to the method of Bowlus and Nieuwland.[2] The acetic acid and acetic acid–boron fluoride compound were weighed into a 250-cc. glass bottle.

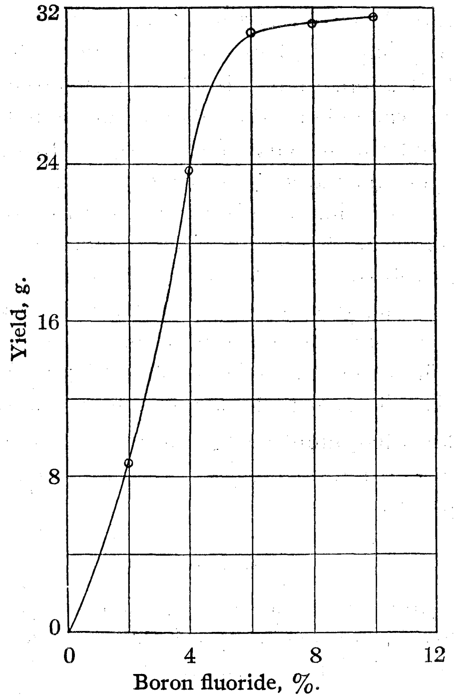

Fig. 1.

The percentage of boron fluoride used was calculated on the basis that the sum of the weight percentages of acetic acid and of boron fluoride was equivalent to 100%. One-third of a mole of cyclohexene,[3] b. p. 82°, distilled twice through a 45-cm. Widmer column, was weighed separately and then added to the acetic acid–boron fluoride mixture in the glass bottle. The reaction bottle was sealed and immediately put into a thermostatically regulated oil-bath kept at a temperature of 80 ± 0.5°. The reaction time was varied from fifty to two hundred and twenty hours. Upon the elapse of time the reaction bottle was removed from the bath and cooled to room temperature. Then the bottle was opened and the contents weighed in order to check whether any loss due to leakage had occurred. The mixture was neutralized with saturated sodium carbonate solution and the upper layer separated (all residues were collected in ether and added to the upper layer). After the ester and cyclohexene layer was washed with water and dried over calcium chloride the mixture was fractionated carefully and the fraction boiling at 175° was collected as the ester. Upon the removal of the ester fraction the temperature rose rapidly and the distillation was discontinued. The quantity of residue varied from 1.5 to 8.9 g. depending upon the quantity of boron fluoride used. The following yields for the varying amounts of boron fluoride, substantially unchanging with time, were obtained. The apparent equilibria were plotted against the percentage boron fluoride as shown in Fig. 1.

TABLE I

BF$_3$, %	2	4	6	8	10	15	18
Yield, g.	8.1–8.8	23.5–23.8	30.7–31	31.3	31.6	31.9[a]	29.3[a]

[a] Diminishing slowly with time.

The solubility of boron fluoride in cyclohexyl acetate was determined by slowly passing boron fluoride into 0.868 mole of the ester. After a period of eleven hours it was found that 0.882 mole of the boron fluoride was absorbed. Heat was liberated during the absorption of the boron fluoride; however, as the quantity of boron fluoride reached a mole per mole ratio with the ester the mixture gradually cooled to room temperature. The absorption also became extremely slow as the molar ratio was reached.

Discussion

It had been noticed throughout the purifications that the quantity of residue obtained from the individual runs having concentrations of boron fluoride equivalent to 10% and less ranged between 1.5 and 1.9 g. Beyond these concentrations of boron fluoride the quantity of residue increased rapidly. This indicates that higher concentrations of boron fluoride rapidly effects polymerization. In addition it was found that one mole of boron fluoride was absorbed by one mole of cyclohexyl acetate. Thus when a sufficient quantity of ester was produced with the lower concentrations of boron fluoride the boron fluoride was made inactive by absorption in the ester. Thereupon the yield of ester remained constant for that particular percentage of boron fluoride giving the appearance of an equilibrium. As higher percentages of boron fluoride were used

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(1) Brunel, *Ann. chim. anal.*, [8] **6**, 216 (1905).

(2) Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

(3) Dehn and Jackson, *ibid.*, **55**, 4285 (1933).

these equilibria approached one another until a maximum was reached. Beyond this point polymerization occurred with a prolongation of reaction time and the yield of ester subsequently decreased.

An explanation for this gradual approach to a maximum is offered on the basis of the following considerations: that the concentration of boron fluoride necessary for bringing about a reverse of the condensation reaction having a reaction velocity equal to that of the condensation reaction, is greater than that used for the condensation itself. Thus in those reactions where low concentrations of boron fluoride are used a state is reached in which the boron fluoride is absorbed by the ester and the concentrations are not sufficient to effect a reversal having a velocity equal to the condensation velocity. As the concentration of boron fluoride is increased in the ester the velocity of the reverse reaction is increased. When the proper amount of boron fluoride is present the velocity of the reverse reaction is equivalent to the velocity of the condensation reaction: there being sufficient boron fluoride on both sides of the reaction to cause the reverse and condensation reactions to proceed with equal velocities. Beyond this concentration of boron fluoride polymerization is more pronounced.

Summary

The influence of time and concentration of boron fluoride upon the condensation of acetic acid with cyclohexene at a constant temperature has been studied. The concentration of boron fluoride is shown to have a marked effect upon the quantity of ester obtained. An explanation was offered for the change in apparent equilibria with the quantity of boron fluoride used.

NOTRE DAME, INDIANA RECEIVED MARCH 11, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Sulfur Studies. XI. Some Sulfur Derivatives of Benzaldehyde

BY J. H. WOOD AND R. W. BOST

Practically nothing is known about monomeric thioaldehydes since they polymerize immediately upon formation. However, the conditions under which they are formed profoundly influence the nature of the resulting polymerization and we have found that reactions by which one would expect to obtain monomeric thiobenzaldehyde lead to a variety of compounds such as the thioester, the mercaptan, the dithio acid, the disulfide, the cyclic trimer, and other polymers. It is the purpose of this paper to describe some of these reactions and to offer a mechanism for the formation of some of the compounds obtained.

Benzal chloride and sodium sulfide react in alcoholic solution to form monomeric thiobenzaldehyde, C_6H_5CHS. However, the compound cannot be isolated and it immediately undergoes polymerization or side reactions. A part polymerizes to β-trithiobenzaldehyde. Some undergoes the Cannizzaro reaction to give benzyl mercaptan, dithiobenzoic acid, and a small amount of benzyldithiobenzoate. A portion of the mercaptan then reacts with thiobenzaldehyde to form a small quantity of benzyl mercaptal of benzaldehyde.

It has been suggested that the Cannizzaro reaction proceeds through ester formation. Our work confirms this belief. That is, thiobenzaldehyde readily undergoes polymerization to dithiobenzoate, and in the presence of alkalies such as sodium sulfide, the ester is saponified to the thio alcohol and dithio acid. On the other hand, the Cannizzaro reaction involving thiobenzaldehyde can be arrested at the ester stage provided that the monomer is formed under conditions which do not produce saponification of the ester. This is accomplished by depolymerizing β-trithiobenzaldehyde by distilling it at 3 mm. in the presence of a few drops of sulfuric acid. A part of the monomer in the distillate immediately re-polymerizes to the trimer and the rest polymerizes to the ester. The Cannizzaro reaction can then be completed from this point if desired by adding sodium sulfide whereupon the thio acid and thio alcohol are immediately formed.

While β-trithiobenzaldehyde is mainly depolymerized by distilling at low pressure in the presence of sulfuric acid, some decomposition also occurs with the formation of stilbene and sulfur. Some tetraphenylthiophene is also formed by the interaction of stilbene and sulfur. When the distillation is carried out in the absence of sulfuric acid, decomposition into stilbene and sulfur with the resultant formation of tetraphenylthiophene is the main course of the reaction rather than depolymerization.

When hydrogen sulfide is passed into an alcoholic solution of benzaldehyde previously saturated with dry hydrogen chloride, trithiobenzaldehyde is formed exclusively.[1] By reducing the acid concentration other types of polymers, perhaps linear, are obtained in the form of pink gums along with varying quantities of the trimer. The pink gum cannot be purified by recrystallization or by vacuum distillation. The latter brings about complete decomposition, mainly into stilbene and sulfur. The monomer does not undergo the Cannizzaro reaction in acid solution.

Hydrogen sulfide reacts with benzaldehyde in the presence of small amounts of potassium hydroxide or sodium hydroxide to form thiobenzaldehyde. Most of the thiobenzaldehyde immediately polymerizes to form a viscous, pink oil; the remainder undergoes the Cannizzaro reaction. Upon distillation *in vacuo*, the pink oil is decomposed to form mostly stilbene and sulfur. However, some benzyl dithiobenzoate also is formed which indicates slight depolymerization.

Fromm and Forster[2] report the preparation of benzyl dithiobenzoate by refluxing an alcoholic solution of C_6H_5CSSNa and sodium hydroxide with an excess of benzyl chloride. They describe the ester as being white prisms, m. p. 55°. Since the other known esters of dithiobenzoic acid are red oils, we repeated the work of Fromm and Forster and obtained in good yield benzyl sulfide, m. p. 50°, instead of the ester. The sulfide was identified by conversion into the sulfone by the method of Bost, Turner and Norton.[3] One would not expect to obtain the ester under the experimental conditions specified by Fromm and Forster since as rapidly as the ester was formed, it would be saponified by the sodium hydroxide, at the elevated temperature, with the formation of C_6H_5CSONa and $C_6H_5CH_2SNa$. The mercaptide would then react with the excess benzyl chloride to form benzyl sulfide. By modifying the experimental conditions, we have obtained the ester in good yield as a red oil, b. p. 179–180° at 3 mm.

Experimental Work

The Reaction of Sodium Sulfide and $C_6H_5CHCl_2$.—Seven and eight-tenths grams of sodium sulfide and 16.1 g. of $C_6H_5CHCl_2$ were dissolved in 125 cc. of anhydrous ethyl alcohol and allowed to stand at room temperature in an atmosphere of nitrogen for a week or longer. A red supernatant liquid and a white precipitate resulted. The same results were also obtained by refluxing six to eight hours. After the reaction was complete, the precipitate was filtered off in an atmosphere of nitrogen and later showed to be sodium chloride and β-trithiobenzaldehyde. A search was made immediately for the monomeric thiobenzaldehyde in the red alcoholic solution. This was done by examining a portion with 2,4-dinitrophenylhydrazine (since benzal chloride, the oxobenzaldehyde, and the thiobenzaldehyde all give the same hydrazone, the first two compounds would interfere with the test and their presence or absence had to be determined); by testing for a thiocarbonyl group with Grote's reagent;[4] and by a fractional vacuum distillation with the subsequent identification of the compounds thus obtained. Benzyl mercaptan and benzyl dithiobenzoate were identified in the distillate. No monomer of thiobenzaldehyde was isolated. The remaining red alcoholic solution was examined as follows: an equal volume of 4% aq. sodium hydroxide solution was added and the whole was then extracted with benzene. Dithiobenzoic acid was isolated from the aqueous portion. The benzene extract was permitted to evaporate spontaneously and the residue was then recrystallized from ethyl alcohol. Benzyl disulfide, benzyl mercaptal of benzaldehyde, and benzyl dithiobenzoate were identified in this portion.

The Reaction of Benzaldehyde and Hydrogen Sulfide in the Presence of Acids.—Hydrogen sulfide passed into an alcoholic solution of benzaldehyde previously saturated with dry hydrogen chloride gives exclusively trithiobenzaldehyde. We have tried varying concentrations of hydrogen chloride from a few bubbles to complete saturation with the hope of finding an acid concentration in which the monomeric thiobenzaldehyde would be stable. The runs were carried out by saturating 5 cc. of benzaldehyde in 20 cc. of absolute ethyl alcohol at −5° with hydrogen sulfide. A few bubbles of dry hydrogen chloride were then passed in while the passage of hydrogen sulfide was continued. An intense blue color formed and rapidly faded with the formation of a sticky white precipitate and a pink gum. Upon increasing the quantity of hydrogen chloride the blue color faded more rapidly. The sticky white precipitate was soluble in benzene from which it was deposited as a pink gum upon complete evaporation of the benzene. Some trithiobenzaldehyde also was formed. Other runs were carried out at room temperature with the same results. Other runs were carried out in which sulfuric acid, zinc chloride, acetic acid, magnesium perchlorate, and phosphorus pentoxide were substituted for hydrogen chloride and gave results identical with above.

The Action of Hydrogen Sulfide upon Benzaldehyde in Presence of Potassium Hydroxide.—Concentration: 0.5 g. KOH; 20 cc. C_6H_5CHO; 100 cc. absolute ethyl alcohol. Hydrogen sulfide was passed in at room temperature for

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(1) E. Baumann and E. Fromm, *Ber.*, **22**, 2600 (1889).

(2) E. Fromm and Forster, *Ann.*, **394**, 340 (1912).

(3) R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

(4) I. W. Grote, *J. Biol. Chem.*, **93**, 25 (1931).

four days. A large quantity of a viscous, pink oil separated during this time and the alcohol layer was colored red. Benzyl mercaptan was identified as one of the products of the reaction by vacuum distillation of a portion of the red alcohol layer. The mercaptan thus obtained was converted into the benzyl 2,4-dinitrophenyl thioether by the method of Bost, Turner and Norton.[3] To the remaining red alcohol layer, an equal volume of 4% aq. sodium hydroxide was added whereupon benzyl disulfide precipitated and was filtered off. The aqueous solution was acidified with hydrochloric acid and then extracted with benzene. The red benzene extract was shaken with lead acetate solution. A precipitate formed which was recrystallized from hot toluene. Red needles resulted, m. p. 205°, which were lead dithiobenzoate.

Vacuum Distillation of Pink Oil.—A special distilling apparatus had to be used in this work due to the fact that a number of compounds distilled over together once depolymerization or decomposition began, and some of these compounds were solids which immediately solidified in the side-arm. The side-arm of the distilling flask had an inside diameter of 2 mm. and at a distance of about 15 mm. from the neck was bent downward so as to make a vertical connection with a bulb to receive solids and high boiling liquids. A horizontal connection at the bend led to an ice trap to condense the more volatile components. All connections and joints were made of ground glass. The neck was a separate piece with ground glass connections so as to permit the use of different size distilling bulbs. An oil-bath was used to heat the distilling flask. The pressure was 3 mm. Decomposition started at about 120° with a change of color to deep red. Heating was continued to 200°. The following compounds were identified in the distillate: benzyl mercaptan, benzyl disulfide, stilbene, and benzyl dithiobenzoate. The mercaptan was in the more volatile portion. The disulfide, stilbene, and the ester distilled over together and had to be separated by fractional recrystallization from ethyl alcohol. The residue left in the distilling flask was recrystallized from ethyl alcohol and gave sulfur and tetraphenylthiophene.

Vacuum Distillation of β-Trithiobenzaldehyde.—The distillation was carried out in the apparatus described above and at a pressure of 3 mm. Depolymerization and decomposition started upon melting (225°). Sulfur, stilbene, tetraphenylthiophene, a few drops of benzyl dithiobenzoate, and a few drops of benzaldehyde were identified as the decomposition products.

Sulfuric acid catalytically depolymerizes paraldehyde and we have attempted to do the same with β-trithiobenzaldehyde. Ten grams of the trimer and 3 drops of concd. sulfuric acid were distilled at a pressure of 3 mm. β-Trithiobenzaldehyde and benzyl dithiobenzoate were the main products of distillation. A few drops of benzaldehyde and a small quantity of stilbene were also formed. Depolymerization instead of decomposition undoubtedly occurred in this distillation since the large quantities of stilbene, sulfur, and tetraphenylthiophene were not formed as was the case of the distillation carried out in the absence of sulfuric acid. However, the distillate immediately polymerized to the trithiobenzaldehyde, or underwent the Cannizzaro reaction.

Another vacuum distillation of the trimer in which phosphoric acid was used as the depolymerizing agent gave the same results.

Preparation of Benzyl Dithiobenzoate.—When the calculated quantity of benzyl chloride is added to a solution of 5.2 g. of dithiobenzoic acid in 50 cc. of ethyl alcohol and 35 cc. of 10% aq. sodium hydroxide at 80° and shaken, a red oil separates. This oil boils at 179–180° at 3 mm.; decolorizes Feigel's solution; upon standing in contact with concd. ammonium hydroxide for six days gives benzamide, benzyl mercaptan, and hydrogen sulfide. This red oil is benzyl dithiobenzoate. Sulfur found: 26.07%. Calcd.: S, 26.20%.

Saponification of Ester.—Three grams of sodium sulfide was dissolved in 40 cc. of absolute alcohol and 1 cc. of benzyl dithiobenzoate was added. The temperature was about 25°. In a few minutes the bright red color of the ester had changed to the darker red color of the acid. After a few hours, the reaction seemed to be complete and an equal volume of water was added. No precipitation of the ester occurred showing that the soluble sodium dithiobenzoate and sodium benzyl mercaptide had been formed. The dithio acid was isolated as described previously; the mercaptan was converted into the insoluble benzyl disulfide by bubbling air through a portion of the solution followed by filtration and recrystallization of the disulfide from alcohol. Incidentally, these reactions offer a satisfactory method for identifying benzyldithiobenzoate.

Action of Hydrogen Sulfide upon $(C_6H_5CH{=}NH\cdot HCl)_2\cdot SnCl_4$.—The aldimine stannichloride was prepared by the method of Stephens.[5] Hydrogen sulfide was passed into an alcoholic solution of the salt for twenty-four hours. A transparent plastic substance that melted between 100–110° was obtained. Some pink gum was also formed. No definite products could be isolated.

The work is being continued with certain high molecular weight aromatic aldehydes and also with certain aliphatic aldehydes to see if similar results are obtained.

Summary

1. Reactions designed to produce monothiobenzaldehyde in neutral or acid solutions lead to polymers of varying types depending upon the acid concentration.

2. Reactions designed to produce the monomer in alkaline solution lead to products which are accounted for on the basis of the Cannizzaro reaction.

3. Monomeric thiobenzaldehyde was formed but existed only for a short time in solution.

4. Benzyl dithiobenzoate has been prepared and characterized.

5. Evidence that the Cannizzaro reaction goes through ester formation as an intermediate was obtained.

6. Polymerized thioaldehydes have been depolymerized.

CHAPEL HILL, N. C. RECEIVED MARCH 1, 1937

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[5] H. Stephens, *J. Chem. Soc.*, **127**, 1874 (1925).

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

The Reaction between Sulfur Dioxide and Olefins and Acetylenes. VI.[1] Ascaridole as a Catalyst for the Reaction

BY L. L. RYDEN, F. J. GLAVIS AND C. S. MARVEL

Previous work[2] has demonstrated that oxygen and various peroxides are catalysts for the addition reaction between sulfur dioxide and olefins and acetylenes. In this communication, we report experiments which prove that ascaridole, a naturally occurring terpene peroxide, is a very effective catalyst for the above reaction with olefins of the type $RCH{=}CH_2$, and for certain monosubstituted acetylenes.

The most striking illustration of the effectiveness of ascaridole is furnished in the case of the reactions between sulfur dioxide and olefin derivatives containing carboxyl, cyano, carbethoxy and phenolic groups. Previously[3] it was shown that these types of olefin derivatives did not combine with sulfur dioxide when paraldehyde, which contained peroxides, was used as a catalyst. However, with ascaridole as a catalyst, polysulfones have now been obtained from undecylenic acid, allylacetic acid, allyl cyanide, methyl undecylenate and *o*-allylphenol in good yields. In the case of simple olefins, ascaridole is very effective when the double bond is in the terminal position as in 1-pentene, but does not seem to be superior to other peroxides when the double bond is buried in the molecule, as in 2-pentene and cyclohexene. The polysulfones obtained when ascaridole is used as a catalyst are the same as those obtained with other peroxides.

No catalyst has yet been found which will promote a reaction between a tri- or tetra-substituted olefin and sulfur dioxide. Conjugation of the double bond with a carbonyl group also seems to block the addition reaction, as no polysulfones have yet been prepared from ethyl crotonate, crotonaldehyde, methyl acrylate or acrolein and sulfur dioxide.

Ascaridole seems to be superior to any other catalyst which has been found for promoting the addition of sulfur dioxide to acetylenes. In this series, paraldehyde which contains peroxides catalyzes the same reactions, but to a somewhat less degree. Either catalyst will promote the reaction between sulfur dioxide and acetylenes of the type $RCH_2C{\equiv}CH$, even when R is a normal alkyl group of twelve carbon atoms. Phenylacetylene also adds sulfur dioxide in the presence of either of these catalysts. However, no satisfactory yields of addition products have been obtained from acetylenes of the type $RC{\equiv}CR$ or $R_2CHC{\equiv}CH$ with either of these catalysts.

The synthesis of 1-pentadecyne is reported in the experimental part of this communication.

Experimental

Preparation of the Polymers.—To a mixture of equal volumes of the liquid olefin, olefin derivative or acetylene and liquid sulfur dioxide, were added a little alcohol (to prevent darkening) and some ascaridole. The reaction mixture was placed in a pressure bottle, sealed and allowed to stand at room temperature. Typical experiments with individual compounds are described in Table I. In general, the compounds were isolated as described in previous papers from this Laboratory.

Using the same general experimental conditions described above, it has not yet been possible to obtain polysulfones from oleyl alcohol, allyl bromide, crotonaldehyde, acrolein, methyl vinyl ketone, methyl acrylate, ethyl crotonate, dimethylacetylene, *t*-butylacetylene or cyclohexylacetylene.

Purification and Properties of New Polysulfones.—*o*-Allylanisole polysulfone is soluble in dioxane, and was purified by dissolving it in this solvent and reprecipitating with water. The compound melted to a clear, glassy substance, and did not decompose below 200°.

o-Allylphenol polysulfone is soluble in acetone, ether, ethyl acetate, ethyl alcohol and 0.1 *N* sodium hydroxide solution. It could be reprecipitated from the alkaline solution by addition of acid.

p-Bromoallylbenzene polysulfone is insoluble in all common organic solvents. It was purified by washing with alcohol and ether.

Allylacetic acid polysulfone separated as a white, rubbery polymer in the reaction flask. It was purified by removing some impurities by steam distillation and then dissolving in dioxane and precipitating it by adding water. This polymer is soluble in ethyl alcohol. It can be dissolved in alkali and reprecipitated.

Allyl cyanide polysulfone separated in the reaction flask as a white, insoluble powder. It was purified by washing with alcohol and ether. It was insoluble in all of the common organic solvents which were tried.

Undecylenic acid polysulfone is slightly soluble in alcohol and insoluble in most other common organic solvents.

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[1] For the fifth communication on this subject, see Glavis, Ryden and Marvel, THIS JOURNAL, **59**, 707 (1937).

[2] (a) Seyer and King, *ibid.*, **55**, 3140 (1933); (b) Frederick, Cogan and Marvel, *ibid.*, **56**, 1815 (1934); (c) Staudinger and Ritzenthaler, *Ber.*, **68B**, 455 (1935); (d) Ryden and Marvel, THIS JOURNAL, **58**, 2047 (1936); (e) Fitch, U. S. Patent 2,045,592 (1936).

[3] Ryden and Marvel, THIS JOURNAL, **57**, 2311 (1935).

TABLE I

Unsaturated compound	Used, cc.	SO_2, cc.	Catalyst, cc.		Time of standing, hrs.	Yield of polymers, g.	M. p. of polymers, °C.	Empirical formula	Analysis S, %	
			EtOH	Ascaridole					Calcd.	Found
1-Pentene	5	5	1	0.2	5	4	340	[a]		
2-Pentene	5	5	1	.2	5	0.1	290–300	[a]		
Cyclohexene	5	5	1	.2	5	.2	Above 200	[b]		
Styrene	5	5	1	.2	5	.5	185–190	[c]		
Undecylenyl alcohol	5	5	2	.1	7	7	Above 330	[a]		
o-Allylanisole	5	5	5	.2	8	7	150–160	$C_{10}H_{12}O_3S$	15.1	14.7
o-Allylphenol	5	5	5	.2	4	4	120–160	$C_9H_{10}O_3S$	16.1	15.8
p-Bromoallylbenzene	10	10	2	.2	12	16.5	255	$C_9H_9BrO_2S$	12.2	12.0
Allylacetic acid	5	5	5	.4[d]	4	5	180–230	$C_5H_8O_4S$	19.5	18.8[e]
Allyl cyanide	10	10	2	.2	12	1	222	$C_4H_5NO_2S$	24.45	24.57
Undecylenic acid	5	5	5	.2	1	5.5	255–275	$C_{11}H_{20}O_4S$	12.9	10.2[f]
Methyl undecylenate	5	5	5	.2	10	5		$C_{12}H_{22}O_4S$	12.2	11.81, 11.9[g]
1-Pentyne	10	10	5	.2	10	8	203–208	[h]		
Phenylacetylene	5	5	3	1	1	5	250–275	[h]		
1-Nonyne	6	5	1	0.2	3	2.4	160–169	[a]		
Cyclohexylpropyne	10	10	2	.2	3	15	110–145	$C_9H_{14}O_2S$	17.2	17.5
1-Pentadecyne	5	5	1	.2	5	3.5	120–140	$C_{15}H_{28}O_2S$	11.7	11.5[i]

[a] For the analysis of this compound, see ref. 2d. [b] For the analysis of this compound, see ref. 2b. [c] For the analysis of this compound, see ref. 1. [d] 0.2 cc. of ascaridole was added when the reaction mixture was made up, and after two hours, a second portion of 0.2 cc. was added. [e] Calcd. for $C_5H_8O_4S$: C, 36.6; H, 5.9. Found: C, 37.5, 37.7; H, 4.86, 4.91. [f] Calcd. for $C_{11}H_{20}O_4S$: C, 53.4; H, 8.06. Found: C, 55.4; H, 8.03. [g] This material was prepared and characterized by Mr. S. Jack Davis. Calcd. for $C_{12}H_{22}O_4S$: C, 54.91; H, 8.46. Found: C, 55.48; H, 7.95. [h] For the analysis of this compound, see ref. 3. [i] Calcd. for $C_{15}H_{28}O_2S$: C, 66.0; H, 10.3. Found: C, 64.6; H, 10.1.

It dissolves in 2% sodium hydroxide solution and reprecipitates on acidification. It is a soft, rubbery mass, very difficult to purify, and hence the analyses were somewhat unsatisfactory.

Methyl undecylenate polysulfone is a very soft, glass-like product which is soluble in hot alcohol, but insoluble in the cold. It was purified by dissolving in hot alcohol and allowing to cool. It was finally washed with hot petroleum ether and dried in a vacuum desiccator. The compound is very soluble in acetone and slightly soluble in chloroform, benzene, ether, dioxane, carbon disulfide and carbon tetrachloride. The product gradually becomes sticky as the temperature is raised, and decomposes completely at 230–250°.

1-Pentadecyne polysulfone is a soft, wax-like product soluble in hot acetone and insoluble in the cold.

2-Bromo-1-pentadecene.—A solution of 0.33 mole of lauryl-magnesium bromide in 200 cc. of dry ether was added to 0.3 mole (59 g.) of bromoallyl bromide, and the reaction mixture was worked up as described by Lespieau and Bourguel[4] for the preparation of cyclohexylbromopropene. The yield of product was 22 g., b. p. 145–155° (3–4 mm.); $n^{20}D$ 1.4670; $d^{20}{}_4$ 1.032.

Anal. Calcd. for $C_{15}H_{29}Br$: C, 62.3; H, 10.03. Found: C, 61.3; H, 10.95.

1-Pentadecyne.—Twenty-five grams of 2-bromo-1-pentadecene was added to a solution of 0.3 mole of sodamide in liquid ammonia.[5] The ammonia was allowed to evaporate, and the residue was treated with water, then dilute hydrochloric acid. The acetylene was taken up in ether and distilled. The yield was 2 cc. of material boiling at 112–113° (5 mm.); $n^{20}D$ 1.4410; $d^{20}{}_4$ 0.8261.

The mercury derivative, prepared by the procedure of Johnson and McEwen,[6] melted at 93°.

Anal. Calcd. for $C_{30}H_{56}Hg$: Hg, 32.6. Found: Hg, 32.1.

Summary

Ascaridole has been shown to be an active catalyst for reaction between sulfur dioxide and olefins of the type $RCH{=}CH_2$, and sulfur dioxide and acetylenes of the type $RC{\equiv}CH$.

o-Allylanisole, *o*-allylphenol, *p*-bromoallylbenzene, allylacetic acid, allyl cyanide, undecylenic acid, methyl undecylenate and 1-pentadecyne, when treated with sulfur dioxide in the presence of ascaridole, give good yields of polysulfones.

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[4] Lespieau and Bourguel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 180.

[5] Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

[6] Johnson and McEwen, *ibid.*, **48**, 469 (1926).

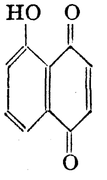
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Addition of Dienes to Halogenated and Hydroxylated Naphthoquinones

BY LOUIS F. FIESER AND J. T. DUNN

The chief purpose of this investigation was to explore further the possibility of synthesizing derivatives of phenanthrene by the addition of dienes to ortho quinones of the naphthalene series. While attempts to utilize β-naphthoquinone itself in the Diels–Alder reaction have not been attended with success, possibly because of the extremely sensitive character of the quinone, it was found[1] that 2,6-dimethyl-3,4-naphthoquinone adds 2,3-dimethylbutadiene very smoothly, a methyl group attached to the active double bond of the quinone effecting a stabilization of this component without offering too great hindrance to the addition. It was thought that other substituted β-naphthoquinones might possess sufficient stability to survive under the conditions required for the addition, possibly even when the substituents are located in the benzenoid ring. 6-Bromo-1,2-naphthoquinone was found in an investigation with Hartwell[2] to be less sensitive than β-naphthoquinone and better adapted to a study of the reactions with diazomethane derivatives, and in a preliminary experiment Dr. Hartwell found that dimethylbutadiene reacts fairly readily with this quinone.[3] With this encouragement, we undertook a study of hydroxylated compounds of a type which would yield polynuclear substances of considerable interest. The condensation of 7-hydroxy-1,2-naphthoquinone with vinylcyclopentene, for example, might afford a 7-hydroxy-1,2-cyclopentenophenanthrene derivative having some features of the oestrone structure. Both 6- and 7-hydroxy-1,2-naphthoquinone were prepared for the purpose in a very satisfactory condition of purity, but the compounds decomposed badly in attempted condensations with the reactive 2,3-dimethylbutadiene and no addition products were isolated.

While the difficulty seemed to be associated chiefly with the tendency of the quinones to undergo decomposition before addition could occur, we thought it worth while to determine whether a hydroxyl group *per se* influences the reaction adversely. In order to establish this point, a few hydroxyl derivatives of α-naphthoquinone were studied under comparable conditions, and it was found that the addition reaction becomes definitely slower with the progressive introduction of hydroxyl groups. Nearly all of the para quinones studied can be condensed satisfactorily with dienes in absolute alcoholic solution at 100° when highly purified products are used, but the time required for complete addition, as indicated fairly accurately by the fading of the original color and by crystallization tests, differs considerably. The addition product of juglone (I) was obtained in 95% yield after heating for twenty minutes, while with naphthazarin (II) a comparable yield (83%) was obtained only after heating for six hours. Naphthopurpurin reacts still more slowly (33% yield in sixty hours), and it was found that addition does not occur to the form which is regarded[4] as the predominant tautomer, IIIa, for water is not eliminated as with 2-hydroxy-1,4-naphthoquinone;[1b] addition occurs rather to the tautomer (IIIb) having an unsubstituted quinonoid nucleus. It is interesting that the acetylation of naphthopurpurin with sulfuric acid as catalyst also proceeds through the form IIIb, for the product is identical with 5,6,8-triacetoxy-1,4-naphthoquinone, prepared[5] from 1,4,5,8-naphthodiquinone by the Thiele reaction. This triacetate



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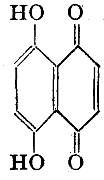
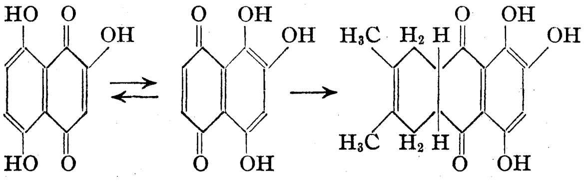


II



IIIa IIIb IV

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(1) (a) Fieser and Seligman, THIS JOURNAL, **56**, 2690 (1934); (b) *Ber.*, **68**, 1747 (1935).

(2) Fieser and Hartwell, THIS JOURNAL, **57**, 1479 (1935).

(3) The crude product (45% yield) apparently suffered oxidation during crystallization from alcohol–benzene and acetic acid, for analysis of the material, m. p. 237–238°, dec., indicated the formula $C_{16}H_{13}O_2Br$ (found: C, 60.8, 60.6; H, 3.90, 3.75).

(4) Fieser, THIS JOURNAL, **50**, 439 (1928).

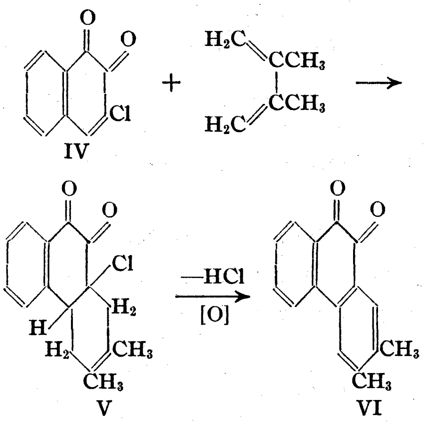
(5) Zahn and Ochwat, *Ann.*, **462**, 72 (1928).

of IIIb adds dimethylbutadiene more slowly (twenty-seven hours) than the diacetate of naphthazarin (three hours).[6] The acetyl derivatives react considerably more rapidly than the corresponding di- and trihydroxyquinones, while juglone appears to add dienes slightly more readily than its acetate. 2-Methyl-8-hydroxy-1,4-naphthoquinone[7] reacts smoothly with dimethylbutadiene, as in comparable cases,[1] and the methyl group merely retards addition.

It is evident from these results that the additive power of a naphthoquinone for dienes is diminished by the presence of hydroxyl groups in the benzenoid nucleus. A lower reactivity of the hydroxylated compounds is manifested also in the Thiele reaction. Dimroth and Roos[8] found it necessary to allow ten days for the completion of the reaction of diacetylnaphthazarin with acetic anhydride–sulfuric acid, and a similar observation concerning acetyljuglone was made in the course of the present work. The marked influence of substituent hydroxyl groups at a considerable distance from the ethylenic linkage involved in the additions is rather surprising. It may be significant that in this series of quinones the additive ability parallels the oxidation–reduction potentials,[4] the compounds of inferior additive propensity being those of low potential.

Since the hydroxylated β-naphthoquinones studied seemed unsuitable for use in the Diels–Alder reaction both because they lack the requisite stability and because of the adverse influence of this type of substituent group, we turned to another line of attack which was suggested by the observation, cited above, that a 3-methyl group stabilizes a 1,2-naphthoquinone and renders it capable of reacting with dienes in very satisfactory fashion. It occurred to us that the same beneficial influence might be exerted by substituents capable of being subsequently eliminated, and we consequently investigated the 3-chloro and 3-bromo derivatives of β-naphthoquinone, and later included the 4-chloro and the 3,4-dichloro compounds in the study. It has been reported already in the patent literature[9] that dienes add to 2-chloro- and 2,3-dichloro-1,4-naphthoquinone, and that hydrogen chloride can be eliminated from the addition products with aromatization of the new ring. We found that the halogenated ortho quinones add dimethylbutadiene very readily in pure chloroform or tetrachloroethane solution, the fading of the color from red to yellow providing a reliable indication of the course of the reaction. To obtain satisfactory results it is essential to prepare the quinones in a state of high purity and to employ pure solvents. Alcohol has a deleterious effect, and even the small quantity present in commercial chloroform brings about extensive decomposition.

3-Chloro-1,2-naphthoquinone reacts with dimethylbutadiene in chloroform solution to an appreciable extent at room temperature, and at 100° the reaction is complete within one hour. A further change occurring under more drastic conditions will be described in another paper. For the isolation of the normal addition product, V, it was necessary to avoid overheating during both the preparation and the recovery of the material. The crude product was obtained as an oil and, once seed was secured, the crystalline substance could be prepared in 70% yield. The pure substance forms pale yellow needles, m. p. 87–88°, but it cannot be preserved for more than a few hours before decomposition sets in. The compound loses hydrogen chloride very readily and the dihydrophenanthrenequinone first formed undergoes oxidation in the air to the phenanthrenequinone VI, or to the quinhydrone. 2,3-Dimethylphenanthrenequinone (VI) can be obtained in excellent yield by the action of alcoholic sodium acetate solution on either the crude or crystalline addition product. With the use of the halogenated quinone, it is thus possible to utilize



IV

V

VI

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[6] Dieterle, Salomon and Nosseck, *Ber.*, **64**, 2086 (1931), describe the addition of piperylene to diacetylnaphthazarin, the reagents being heated for five hours at 100° in alcoholic solution. The addition of dienes to naphthazarin in benzene solution is reported in the patent literature [see *Chem. Zentr.*, **101**, II, 808 (1930); **102**, I, 2938 (1931)].

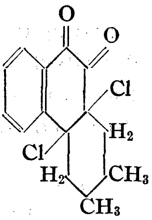
[7] Fieser and Dunn, THIS JOURNAL, **58**, 572 (1936).

[8] Dimroth and Roos, *Ann.*, **456**, 177 (1927).

[9] I. G. Farbenindustrie, English Patent 320,375 (1929) [*Chem. Zentr.*, **101**, II, 808 (1930)].

the Diels–Alder reaction for the synthesis of phenanthrene derivatives in satisfactory yield.

3-Bromo-1,2-naphthoquinone behaves much like the corresponding chloro compound. 4-Chloro-1,2-naphthoquinone is less stable in solution than the 3-isomer, and, as the addition proceeds much more slowly, the compound is not well suited to synthetic uses. The addition product was not isolated but converted in the crude state into VI. The two halogen atoms of 3,4-dichloro-1,2-naphthoquinone seem to hinder the addition to a considerable degree, for the color faded to an appreciable extent only after heating the mixture for three days at 100°. The addition product (VII), isolated as a crystalline solid, is much more stable than the monochloro compound V, probably because the hydrogen atoms adjacent to the halogens are not located on bridge carbon atoms. The substance is attacked only slowly by dilute alcoholic alkali at the boiling point.



VII

Experimental Part[10]

1. Preparation of Hydroxynaphthoquinones

6-Hydroxy-1,2-naphthoquinone[11] was prepared by the method of Dimroth and Kerkovius,[12] the average yield (pure) from 2,6-dihydroxynaphthalene being 31.5%. Reduction of the benzeneazo compound with sodium hydrosulfite gave less satisfactory results. It was found advantageous to use a small amount of stannous chloride as an antioxidant in the crystallization of both the starting material and 1-amino-2,6-dihydroxynaphthalene hydrochloride. The quinone formed bronze-red leaflets from dilute acetone, dec. about 165°. Attempts to isolate products of the reaction of the substance with 2,3-dimethylbutadiene and with diazomethane were unsuccessful, the quinone undergoing extensive decomposition. An acetyl derivative could not be obtained with the use of sodium acetate or in pyridine solution; in the presence of sulfuric acid catalyst, the quinone undergoes the Thiele reaction.[12]

7-Hydroxy-1,2-naphthoquinone was prepared from 2,7-dihydroxynaphthalene by the standard procedure described by one of us,[13] using sulfanilic acid rather than aniline[12] as the coupling component, and reducing the dye with sodium hydrosulfite. For the preparation of 2,7-dihydroxynaphthalene, technical "naphthalene-2,7-disulfonic acid" (220 g.) was crystallized with calcium chloride (equivalent to 55 g. of anhydrous material) from water (250 cc.), and after a further crystallization using Norite the dried, colorless calcium salt (134 g.) was fused with 500 g. of potassium hydroxide and 10 cc. of water, initially at 200° and finally at 300°. The slightly cooled melt was ladled into ice and hydrochloric acid, the material was brought into solution at the boiling point, using sufficient acid to decompose any calcium bisulfite and, after decolorizing with Norite and cooling, the product separated as large colorless needles in 66% yield, based on the purified calcium salt. To obtain 7-hydroxy-1,2-naphthoquinone satisfactorily it is essential to use pure, colorless, 1-amino-2,7-dihydroxynaphthalene hydrochloride (recrystallized in the presence of stannous chloride), to add the ferric chloride to the solution of this substance all at once with efficient mixing, and to collect the product rapidly as soon as the crystals separate. The quinone, obtained as dark red microcrystals, melting at 203–204°, dec., in 30% yield from the dihydroxy compound, could not be recrystallized without undergoing decomposition. The behavior in attempted reactions was like that of the isomer.

Juglone.—We attempted without success to convert 1,5-dihydroxynaphthalene into the 4-amine through the *p*-sulfobenzeneazo compound, and eventually adopted the oxidation method of Willstätter and Wheeler.[14] The 1,5-dihydroxynaphthalene was conveniently precipitated from alcohol with water, washed, and added to the dichromate mixture in the form of a thin paste. The juglone extracted with petroleum ether was further purified by crystallization from alcohol and the yield of material melting at 153–154° was 15%. **Acetyljuglone** was prepared more satisfactorily than described by Bernthsen and Semper[15] by adding 2 drops of concentrated sulfuric acid to a suspension of 0.25 g. of juglone in 2 cc. of acetic anhydride, stirred in an ice-bath. The solid soon dissolved, and after cautiously decomposing the excess anhydride with water and adding more water at the boiling point, the acetyl compound crystallized as yellow plates (0.3 g., 97%). Recrystallized from alcohol, it formed yellow needles, m. p. 153–154°.

1,2,4,5(or 8)-Tetraacetoxynaphthalene was obtained by suspending 1 g. of powdered juglone in a cold solution of 4 drops of concentrated sulfuric acid in 8 cc. of acetic anhydride and allowing the mixture to stand with occasional shaking for ten days. The quinone dissolved, the color of the solution faded and colorless crystals of the product separated. After treatment with water, the crude product (1.4 g., 68%) was crystallized from alcohol, forming clusters of colorless prisms, m. p. (camphor-like) 154°.

Anal. Calcd. for $C_{18}H_{16}O_8$: C, 59.98; H, 4.48. Found: C, 60.37; H, 4.67.

2,5(or 8)-Dihydroxy-1,4-naphthoquinone was obtained by hydrolyzing the tetraacetate with 25% methyl alcoholic potassium hydroxide, oxygenating the solution, and acidifying an aqueous solution of the red salt which separated. The crystalline precipitate (76% yield) separated from aqueous acetone as clusters of lemon yellow microcrystals,

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[10] The melting points are uncorrected.

[11] Kehrmann, *Ber.*, **40**, 1960 (1907).

[12] Dimroth and Kerkovius, *Ann.*, **399**, 36 (1913).

[13] Fieser, *Org. Syntheses*, **17**, 9, 68 (1937); L. F. Fieser and M. Fieser, THIS JOURNAL, **57**, 491 (1935).

[14] Willstätter and Wheeler, *Ber.*, **47**, 2796 (1914).

[15] Bernthsen and Semper, *ibid.*, **18**, 203 (1885).

dec. about 220°. The properties corresponded to those of the oxidation product of juglone obtained by Mylius.[16]

Naphthazarin was prepared according to Fieser[4] (using 15% fuming acid) in the yield reported, and purified by repeated crystallization from benzene, when it formed beautiful long deep green needles having a metallic reflex. Less pure material is red and gives inferior results in the Diels–Alder reaction. The diacetate, m. p. 195–196°, was prepared with the acetic anhydride (8 cc.)–sulfuric acid (6 drops) mixture,[17] and it was noted that no appreciable addition of the reagent occurred on heating the solution at 80° for ten minutes.

Naphthopurpurin was prepared according to Fieser[4] and crystallized twice from benzene; small, red needles were obtained in 22.5% yield.

5,6,8-Triacetoxy-1,4-naphthoquinone.—1,4,5,8-Naphthodiquinone was prepared as described by Zahn and Ochwat[5] and crystallized from glacial acetic acid–petroleum ether, taking care to avoid overheating and employing no decolorizing carbon (which causes reduction). Pale yellow crystals were obtained in 40% yield. The above triacetate was prepared from the diquinone as described[5] in 56% yield and it formed yellow prisms from alcohol, m. p. 165–166°. The sample became red on storage. An identical product was obtained in 94% yield by the action of acetic anhydride–sulfuric acid on naphthopurpurin at room temperature; the reaction was complete after warming for a few minutes.

2. Preparation of Halo-β-naphthoquinones

3-Chloro-1,2-naphthoquinone was prepared in 56% yield from β-naphthol through 1,1,3,4-tetrachloro-2-ketotetrahydronaphthalene according to Zincke,[18] and the properties were as reported. **3-Bromo-1,2-naphthoquinone**, m. p. 177–178°, was obtained in 67% yield by the bromination of β-naphthoquinone.[19] The crude **3,4-dichloro-1,2-naphthoquinone** prepared according to Zincke and Engelhardt[20] contained a considerable amount of dark, resinous material which can be removed by liberal washing with ether. The yield of pure product, m. p. 183.5–184.5°, was 45%.

As Zincke's method of preparing **4-chloro-1,2-naphthoquinone**[21] seemed unsatisfactory, an adaptation of Fries and Schimmelschmidt's[22] method of preparing the 3-bromo compound was employed. 1,1-Dichloro-2-ketodihydronaphthalene was prepared[22] from β-naphthol in 55% yield, and rearranged[22] to 1,4-dichloro-2-naphthol, the yield of distilled material, m. p. 121–122°, in this step being 63%. A fine suspension of 14 g. of the dichloronaphthol in 70 cc. of glacial acetic acid was stirred at 15° and treated slowly with 7 cc. of concentrated nitric acid, when the material soon dissolved. After brief cooling at 0° the crystalline 1,4-dichloro-1-nitro-2-ketodihydronaphthalene which separated was collected and washed with dilute acetic acid and then with water. The substance was obtained as pale yellow needles which cannot be preserved for long at room temperature without decomposing; yield, 10 g. (59%). This material (10 g.) was warmed cautiously with 25 cc. of benzene until dissolved and the solution was boiled for a short time to eliminate nitrosyl chloride. On adding ligroin and cooling, dull orange-red needles of 4-chloro-1,2-naphthoquinone separated; m. p. 132–136°, dec.; yield 5.9 g. (80%). It was not found possible to purify the quinone further by crystallization, as some decomposition invariably occurred. On attempting to prepare the hydroquinone diacetate for analysis by reductive acetylation with acetic anhydride, zinc dust and sodium acetate, it was found that the halogen atom is replaced by an acetyl group, the product being 1,2,4-triacetoxynaphthalene, m. p. and mixed m. p. 134–135°; yield 60%.

3. Addition of Dienes to the Hydroxynaphthoquinones

The condensation of the para quinones with dienes seemed to proceed better in absolute alcohol than in other solvents. The amount of alcohol used was more than ample to bring the quinone into solution at the boiling point (see Table I), one-tenth this volume of freshly prepared diene[23] was added, and the tube was sealed and heated in a steam bomb at 100°. The progress of the reaction could be followed sometimes by the fading of the color, although the change usually is not great. A more reliable indication can be obtained by removing and cooling the tube, for the addition products of the para quinones crystallize quite readily and in characteristic form. The heating was discontinued as soon as the change seemed to be complete, and the figures given in the third column of the table represent the approximate times required for completion of the reactions under comparable conditions. The yields recorded refer to purified, crystalline material. Naphthopurpurin-dimethylbutadiene was extracted from the crude reaction product with petroleum ether and recrystallized from this solvent; the other addition products were crystallized from alcohol. Traces of impurities in the starting material seem to promote extensive decomposition during the condensation.

5,9,10 - Triacetoxy - 2,3 - dimethyl - 1,4 - dihydroanthracene was obtained in 67% yield by the action of acetic anhydride and fused sodium acetate on juglone-dimethylbutadiene. The compound formed colorless needles, m. p. 197–198°, from alcohol.

Anal. Calcd. for $C_{22}H_{22}O_6$: C, 69.07; H, 5.80. Found: C, 69.46; H, 6.02.

2,3-Dimethyl-5-hydroxyanthraquinone was prepared by the action of alcoholic potassium hydroxide solution on both the above triacetate and on juglone-dimethylbutadiene. A solution of 0.2 g. of the latter compound in 8 cc. of alcohol was warmed with 1 cc. of 10% aqueous potassium hydroxide solution, crystals of a red salt which separated were dissolved by adding water, and the solution was oxygenated and acidified. Crystallization of the product from alcohol gave glistening yellow needles melting at 178.5–179.5°; yield 0.18 g.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.16; H, 4.80. Found: C, 76.37; H, 4.96.

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[16] Mylius, *Ber.*, **18**, 463 (1885).

[17] Thiele and Winter, *Ann.*, **311**, 341 (1900).

[18] Zincke and Kegel, *Ber.*, **21**, 3540 (1888).

[19] Zincke and Schmidt, *ibid.*, **27**, 733 (1894).

[20] Zincke and Engelhardt, *Ann.*, **283**, 341 (1894).

[21] Zincke and Kegel, *Ber.*, **21**, 3378 (1888).

[22] Fries and Schimmelschmidt, *Ann.*, **484**, 245 (1930).

[23] In preparing 2,3-dimethylbutadiene by the catalytic method,[1a] it has been found expedient to control the rate of distillation of pinacol through the reaction tube to 35 cc. per twenty minutes. Under these conditions there is less high-boiling material (pinacolone) requiring re-passage through the tube and the total yield of redistilled product is increased to 75%.

TABLE I

ADDITION PRODUCTS OF 1,4-NAPHTHOQUINONES WITH 2,3-DIMETHYLBUTADIENE

Quinone	Abs. alc. per g. of quinone, cc.	Time of heating hrs.	Yield, %	Product	M. p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Juglone	22	0.33	95	Faintly yellow needles	141–142	74.97	75.05	6.30	6.59
Acetyljuglone	24	0.5	94	Colorless needles	126–128	72.43	72.77	6.10	6.26
Naphthazarin[24]	55	6	83	Salmon-pink plates	195, dec.	70.56	70.73	5.93	6.18
Diacetylnaphthazarin[24]	88	3	92	Nearly colorless plates	175, dec.	67.38	67.58	5.66	5.93
Naphthopurpurin	44	60	33	Red-brown microcrystals	255, dec.	66.65	66.90	5.60	5.29
5,6,8-Triacetoxy-1,4-naphthoquinone	75	27	70	Pale brown needles	186, dec.	63.74	63.55	5.35	5.87
2-Methyl-8-hydroxy-1,4-naphthoquinone	20	19	84	Colorless blades	78–79.5, dec.	75.53	75.57	6.71	6.59
WITH BUTADIENE									
Juglone	50	0.5	94	Pale yellow needles	124–125	73.99	74.21	5.31	5.60

4. Addition Products of Halogenated β-Naphthoquinones

3 - Chloro - 1,2 - naphthoquinone - 2,3 - dimethylbutadiene.—A mixture of 4 g. of the quinone, 8 cc. of the diene, and 40 cc. of purified chloroform (shaken with concentrated sulfuric acid, washed with water, dried, distilled) was sealed in a tube and heated in a steam-bath with exclusion of light. The tube was shaken vigorously until all solid material had dissolved, for it is generally found that solid particles of a quinone tend to suffer decomposition and initiate the destruction of material in solution. The red color of the solution soon began to fade and in forty-five to fifty minutes changed to yellow. After one hour the solution was cooled, shaken with Norite for ten minutes at room temperature, and the solvent was distilled from the filtered solution in vacuum, keeping the temperature below 60°. The resulting viscous yellow oil could be preserved for some time as such or in ethereal solution without decomposing. Crystalline material eventually was obtained by cooling an ethereal solution in a bath of solid carbon dioxide and adding petroleum ether, and with seed available the crystalline compound was obtained easily. Recrystallized from ether–petroleum ether, the substance formed glistening, lemon yellow needles, m. p. 87–88°; yield, 4 g. (70%).

Anal.[24] Calcd. for $C_{16}H_{15}O_2Cl$: C, 69.92; H, 5.51. Found: C, 69.61; H, 5.37.

A sample of the pure material kept in a vacuum desiccator at 10° showed signs of decomposition within three hours and soon changed to a greenish black amorphous mass. When shaken with air in suspension in either alcohol or ether, this soon changed to an orange powder; on crystallization from glacial acetic acid orange plates of 2,3-dimethylphenanthrenequinone were obtained in 87% yield. The quinone was identified by mixed melting point determination, using for comparison a sample prepared previously in this Laboratory.[25] Both samples melted at 237–238° (242–243°, corr.[26]). When the oily addition product was heated for a few minutes on the steam-bath at reduced pressure, hydrogen chloride was eliminated suddenly and the dark residue yielded the above quinone when digested with solvents. 2,3-Dimethylphenanthrenequinone was obtained in theoretical yield when the oily or crystalline addition product was warmed with alcoholic sodium acetate solution.

3-Bromo-1,2-naphthoquinone.—The reaction with dimethylbutadiene was conducted exactly as above, except that the heating was continued for two hours, and a solution of the oily addition product in 2–3 cc. of glacial acetic acid was treated with a solution of 1 g. of chromic anhydride in 6 cc. of 80% acetic acid. The solution became warm and, on cooling, 2,3-dimethylphenanthrenequinone crystallized in a nearly pure condition; yield, 0.38 g. (76%).

4-Chloro-1,2-naphthoquinone.—Under the conditions specified for the isomer, the addition of dimethylbutadiene proceeded only slowly; the red color faded slowly and then the solution began to darken. Heating was discontinued after seventy-two hours and the crude reddish oil obtained on removing the solvent was taken into ether–petroleum ether. Attempts to obtain crystals of the addition product were unsuccessful, but the solution on standing slowly deposited orange material from which pure 2,3-dimethylphenanthrenequinone was obtained on recrystallization in 15% yield.

3,4 - Dichloro - 1,2 - naphthoquinone - 2,3 - dimethylbutadiene, prepared by heating 3 g. of the quinone, 6 cc. of the diene, and 30 cc. of pure chloroform at 100° for sixty hours, was obtained crystalline from ether–petroleum ether and recrystallized from this solvent pair; yield 1 g. (24%). The compound formed large, pale yellow prisms melting at 130.5–131.5°.

Anal. Calcd. for $C_{16}H_{14}O_2Cl_2$: C, 62.14; H, 4.57. Found: C, 61.82; H, 4.79.

The dichloro compound is not appreciably attacked by short boiling in an alcoholic solution of sodium acetate; boiling 10% alcoholic potassium hydroxide slowly produces a yellow coloration and gives a resinous product.

Summary

Hydroxylation of the benzenoid ring of α-naphthoquinone results in a decrease in the velocity of addition of dienes; similarly substituted β-naphthoquinone derivatives, like the parent compound, are not suitable for use in the diene synthesis.

3-Chloro- and 3-bromo-1,2-naphthoquinone add

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[24] Analyses by Mrs. G. M. Wellwood.

[25] Fieser and Hershberg, THIS JOURNAL, **57**, 2192 (1935).

[26] Determined by Dr. Hershberg with his special apparatus [Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936)]. We are at a loss to account for the lower corrected melting point determined for the earlier sample[25] by applying a stem correction and observed independently by another worker.

2,3-dimethylbutadiene readily and the addition products can be converted smoothly into phenanthrenequinones. Halogen substitution at the 4-position is less favorable to the Diels–Alder reaction.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED MARCH 27, 1937

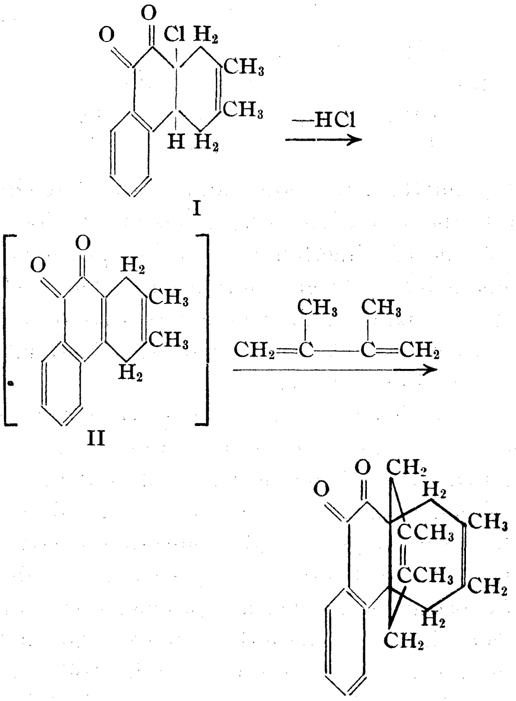
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Further Reaction Product from 3-Chloro-1,2-naphthoquinone and Dimethylbutadiene

BY LOUIS F. FIESER AND J. T. DUNN

In studying the reaction between 3-chloro-1,2-naphthoquinone and 2,3-dimethylbutadiene in chloroform solution at 100°,[1] it was observed that the initially red solution fades to yellow as addition proceeds and that the formation of the halogen-containing addition product (I, below) is complete in slightly less than one hour. When the heating is continued much beyond this point the solution slowly acquires a red color, and this second change occurs particularly rapidly when the hot reaction tube is exposed to direct sunlight. In the presence of excess diene, the red color again fades to yellow and when the changes are finally complete the solution exhibits a greenish fluorescence. The reaction product, isolated from this solution in 36% yield in a nicely crystalline condition, is free from halogen and has the composition of the chloroquinone plus two molecules of dimethylbutadiene, less the elements of hydrogen chloride.

The only plausible interpretation of these observations which we have been able to construct is that the yellow addition product I first loses hydrogen chloride from adjacent, bridge carbon atoms, and that the dihydrophenanthrenequinone II adds a second molecule of the diene at the reactive ethylenic linkage thus established, giving a tetracyclic diketone of the structure III. It is assumed that the dihydrophenanthrenequinone II, being a substituted β-naphthoquinone derivative, is responsible for the transient red color of the solution, and if this explanation is correct the influence of light is to catalyze the formation of this substance from I by the elimination of hydrogen chloride.



I

II

III

Attempts to characterize the unusual reaction product regarded as III were disappointing, as were attempts to establish the structure by degradation. In nearly all reactions tried the first change seemed to consist in a reversal of the Diels–Alder reaction, for the only transformation products isolated were derived from the dihydrophenanthrenequinone II. Perbenzoic acid titration alone gave a positive result, for this indicated the presence of two reactive double bonds, as required for the formula III. When heated somewhat above the melting point (135°), the product decomposed with effervescence and left a dark green residue which underwent air-oxidation in contact with solvents and afforded pure 2,3-dimethylphenanthrenequinone in good yield. This quinone was obtained also on heating the supposed tetracyclic compound in glacial acetic acid solution for twelve hours and, more rapidly and in nearly quantitative yield, by the action of chromic acid on the compound in the same solvent. The tetracyclic product did not absorb hydrogen readily in the presence of Adams catalyst, and

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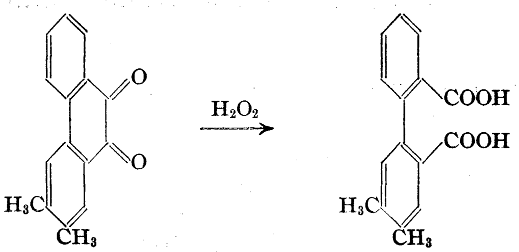
(1) Fieser and Dunn, THIS JOURNAL, **59**, 1016 (1937).

the only product isolated (after exposure to the air) was 2,3-dimethylphenanthrenequinone. Alkaline hydrogen peroxide gave a substance identified as 4,5-dimethyl-2,2′-diphenic acid (V) by comparison of a sample of the acid prepared from 2,3-dimethylphenanthrenequinone by the action of hydrogen peroxide in acetic acid solution.

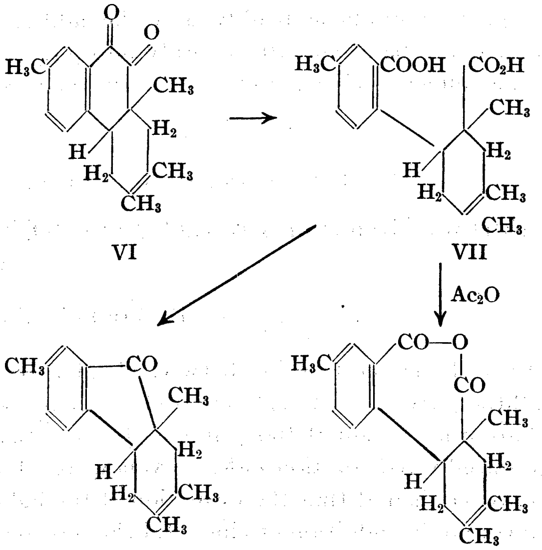


IV V

In all these reactions, and in the Zerewitinoff test, the tetracyclic product seems to lose one molecule of dimethylbutadiene in preference to undergoing other transformations. On attempting to prepare a quinoxaline derivative or a semicarbazone (or acetate), the starting material was recovered unchanged.

Although entirely rigid evidence is not available, the analysis of the new product, the results of titration with perbenzoic acid, and the ready conversion of the substance into 2,3-dimethylphenanthrenequinone all point to the structure III for the compound. Under similar conditions of experiment, an identical product was obtained from 3-bromo-1,2-naphthoquinone. An interesting property of the compound is its ability to exist in the two forms which differ strikingly in appearance. When prepared in the dark and purified with but little exposure to light, the product crystallized in the form of bright yellow prisms. When these were exposed for a short time to direct or diffused sunlight, the yellow color faded and the crystals became very nearly colorless, while retaining the original form. Both modifications have the same melting point.

In the course of the investigation of the tetracyclic diketone III it seemed desirable to determine if any of the peculiarities of this compound are exhibited by the structurally similar addition product VI from 2,6-dimethyl-3,4-naphthoquinone and 2,3-dimethylbutadiene.[2] This is not the case, for the addition compound VI can be distilled in vacuum without loss of dimethylbutadiene; it reacts normally with *o*-phenylenediamine, and yields on catalytic hydrogenation a colorless dihydro derivative possibly similar to that obtained by Smith and Hac[3] from prehnitenequinone-cyclopentadiene. The diketone is cleaved smoothly by alkaline hydrogen peroxide to the dibasic acid VII. The behavior of this tetramethyltetrahydrodiphenic acid on pyrolysis is similar to that of the two perhydrodiphenic acids studied by Vocke.[4] When heated at 300–330°, the acid very slowly loses carbon dioxide and gives a ketone VIII in small yield. The anhydride (IX) can be obtained easily with the use of acetic anhydride, but it does not appear to be formed in the pyrolytic reaction. The behavior of VII therefore accords with the prediction of the Blanc rule and the acid thus differs from those 1,4-dibasic acids derived from steroids in which the acid groups are attached to adjacent rings.



VI VII VIII IX

Experimental Part[5]

1. The Addition Product

2,3-Dimethyl-1,4,11,12-tetrahydrophenanthrenequinone-11,12-endo-2′,3′-dimethylbutene-2′ (III).—A solution of 4 g. of 3-chloro-1,2-naphthoquinone and 16 cc. of 2,3-dimethylbutadiene in 32 cc. of pure chloroform was sealed in a tube and heated in a pan of boiling water with exposure to the sunlight. The red solution became yellow in about forty-five minutes, and after thirty-five to fifty minutes the color changed again to red and this slowly began to fade. After a further period of about two hours the solution had become yellow and acquired a greenish fluorescence. After a total of five hours the tube was cooled, the solution was clarified with Norite, and the sol-

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(2) (a) Fieser and Seligman, THIS JOURNAL, **56**, 2690 (1934); (b) *Ber.*, **68**, 1747 (1935).

(3) L. I. Smith and Hac, THIS JOURNAL, **58**, 229 (1936).

(4) Vocke, *Ann.*, **508**, 1 (1934).

(5) The melting points are uncorrected.

vent was removed on the steam-bath. From a portion of the residual reddish oil seed was obtained with the use of chloroform–petroleum ether by thorough cooling and scratching. A solution of the main product in alcohol slowly deposited crystals on being seeded, and after washing this material free of oil with alcohol and recrystallizing it from alcohol, a pure product was obtained; average yield, 2.4 g. (36%). The compound is very readily soluble in benzene and moderately soluble in alcohol; the solutions ordinarily are colorless but become slightly yellow when exposed to direct sunlight. The solution in glacial acetic acid (readily soluble) becomes yellow on boiling, even without exposure to light. The solutions in alcohol or benzene tend to remain supersaturated, but slowly deposit the compound in the form of large, flat, diamond-shaped prisms which are practically colorless but show a faint tinge of yellow. The melting point is like that of camphor, softening occurring at about 130° with a finely ground sample, and the crystal structure disappearing at 135°. The melt is slightly yellow, but after partial crystallization the sample re-melts at 135°.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.45; H, 7.55. Found: C, 82.43, 82.57; H, 7.56, 7.79.

When the reaction was conducted in the dark, or with but little exposure to light, it was found necessary to continue the heating for sixteen to twenty hours. The reaction product on purification with but little exposure to light crystallized in diamond-shaped prisms similar to those above but having a brilliant yellow color. The melting point was the same as that of the nearly colorless crystals and no depression was observed on mixing the samples. On exposing the yellow prisms to direct sunlight the color faded without change of crystalline form and white crystals, faintly tinged with yellow were obtained. The colorless form seems to be the more stable of the two. A partial reversal occurs when the initially colorless solution of this form in chloroform is exposed to direct sunlight, for the solution acquires a yellowish color and the crystals subsequently deposited are pale yellow.

The compound III was prepared also in a similar manner from 3-bromo-1,2-naphthoquinone and identified by comparison with the above sample. The color changes were less distinct, and heating in the sunlight was conducted discontinuously for a total of thirteen hours; yield 35%.

Titration of III with perbenzoic acid in chloroform solution, conducted by Dr. M. S. Newman, indicated the absorption of 1.7 atoms of oxygen after forty-eight hours and 1.8 atoms after seventy-two hours.

Unsuccessful attempts to prepare derivatives of III and to effect a hydrogenation have been reported above. On heating the compound somewhat above the melting point at 4 mm. pressure, the oil suddenly began to effervesce. When this had ceased, the product was distilled and the glassy distillate was triturated with ether. This gave an orange powder from which pure 2,3-dimethylphenanthrenequinone, m. p. 237–238°, was obtained by crystallization; yield, 72%. A better conversion was obtained by adding 0.25 g. of chromic anhydride in 4 cc. of 90% acetic acid to 0.25 g. of III in 3 cc. of glacial acetic acid. Orange crystals of the quinone soon separated and the total product, collected after adding a little water, amounted to 0.17 g. (91%).

4,5-Dimethyl-2,2′-diphenic Acid (V).—This acid was conveniently prepared by heating a suspension of 1 g. of 2,3-dimethylphenanthrenequinone in 5 cc. of glacial acetic acid with 2 cc. of 30% hydrogen peroxide just below the boiling point until solution was complete and the color had faded to a very pale yellow. On dilution with water, the acid separated as colorless crystals; yield of once recrystallized material, 1 g. (88%). The pure acid separates from dilute acetic acid as clusters of colorless microcrystals, m. p. 203–204°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 70.71; H, 5.49.

The same acid was obtained by warming a mixture of 1 g. of III, 0.7 cc. of 30% hydrogen peroxide solution, 45 cc. of alcohol, and 3 cc. of 10% sodium hydroxide (added in drops) at 50–60° for three hours. The solution was acidified, evaporated to dryness, and the organic material was taken successively into ether, alkali and ether and obtained as clusters of microneedles from ether–petroleum ether (0.75 g.). After repeated crystallization from ether, the product melted at 202–204° and gave no depression with V, above.

2. 2,6-Dimethyl-3,4-naphthoquinone–2,3-Dimethylbutadiene (VI)

The yield in the preparation[2a] of the intermediate 2,6-dimethyl-4-amino-3-naphthol was improved considerably by employing more acid to dissolve the crude amine. The dye from 0.3 mole of the dimethylnaphthol was prepared and reduced exactly as described for the preparation of 1,2-aminonaphthol,[6] and the moist amine was mixed with 800 cc. of water, 45 cc. of concentrated hydrochloric acid, and 0.8 g. of stannous chloride and added to 2.2 liters of boiling water. Solution occurred in forty-five minutes and 200 cc. of concentrated acid was added to the filtrate. The yield of colorless hydrochloride was 62 g. (92%). In conducting the oxidation the amount of acid was increased from 10 cc. to 25 cc.; yield 94%; m. p. (recrystallized), 151–152°.

The addition product VI was obtained in somewhat improved yield (93%) by using 2.9 cc. of dimethylbutadiene and 16 cc. of absolute alcohol per gram of pure quinone, heating the mixture for seventy-five hours at 100°, and crystallizing the product once from dilute methanol.

The quinoxaline derivative, prepared by heating 1 g. of VI and 0.5 g. of *o*-phenylenediamine in 7 cc. of glacial acetic acid on the steam-bath for one hour and crystallizing the product (1.25 g.) from acetic acid, formed yellow plates, m. p. 137–138°.

Anal. Calcd. for $C_{24}H_{24}N_2$: C, 84.66; H, 7.11. Found: C, 84.46; H, 7.44.

A dihydro derivative was obtained by shaking 1 g. of VI dissolved in alcohol and 30 mg. of Adams catalyst with hydrogen, absorption ceasing after five minutes, even when fresh catalyst was added. The product formed colorless needles, m. p. (camphor-like) 131°, from alcohol; yield 0.72 g. The substance dissolves in alcoholic sodium hydroxide solution in the cold to give a pale red solution.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.94; H, 8.21. Found: C, 80.00; H, 8.50.

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[6] Fieser, *Organic Syntheses*, **17**, 9, 68 (1937).

Reduction of VI in alcohol with aqueous hydrosulfite solution gave a colorless product, m. p. 107–108°, which was not further characterized.

2,4,5,4'-Tetramethyl-1,2,3,6-tetrahydro-2,2'-diphenic Acid (VII).—A solution of 2 g. of VI and 1.4 cc. of 30% hydrogen peroxide in 20 cc. of dioxane at 80–90° was treated cautiously with 7 cc. of 10% sodium hydroxide in portions. A vigorous reaction ensued and the yellow color disappeared. Acidified and diluted with 100 cc. of water, the solution slowly deposited needles of good product; yield, 2 g. (92%). The acid is very soluble in dioxane, moderately so in alcohol or ether, very sparingly soluble in benzene. Recrystallization from acetic acid gave small, colorless needles, m. p. 248–249°.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.48; H, 7.34. Found: C, 71.43; H, 7.53.

The dimethyl ester, prepared with diazomethane, formed glistening needles, m. p. 88–89°, from dilute methanol.

Anal. Calcd. for $C_{20}H_{26}O_4$: C, 72.68; H, 7.94. Found: C, 72.66; H, 7.98.

The ester was hydrolyzed completely on being boiled for six hours with 25% potassium hydroxide solution.

The anhydride (VIII) was prepared by refluxing a solution of 0.9 g. of VII in 6 cc. of acetic anhydride for fifteen hours. The solvent was removed in vacuum and the product was crystallized from ligroin, giving 0.45 g. (53%) of nearly pure material. The anhydride forms lustrous, colorless needles from ligroin, m. p. 97–98°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.00; H, 7.09. Found: C, 76.06; H, 7.42.

2,3,7,10-Tetramethyl-1,4,10,11-tetrahydrofluorenone-9-semicarbazone.—The acid VII (0.8 g.) when heated under nitrogen in a bath at 330–33° slowly evolved carbon dioxide. After ten hours the dark residue, which gave no test for anhydride when treated in benzene with aniline, was taken into ether and the solution was extracted with dilute alkali, which gave on acidification 0.65 g. of unchanged acid. The oily residue from the ether was treated in alcohol with semicarbazide solution, heating for three hours on the steam-bath. Some of the semicarbazone crystallized during this period and, after cooling, the total yield was 0.2 g. (22%). The compound forms yellow microcrystals from alcohol; it softens at 244° and melts at 260° with decomposition.

Anal.[7] Calcd. for $C_{18}H_{23}ON_3$: N, 14.14. Found: N, 14.01.

Summary

The product obtained by the addition of 2,3-dimethylbutadiene to 3-chloro-1,2-naphthoquinone loses hydrogen chloride in chloroform solution at 100° and a second molecule of the diene adds to the resulting product giving an interesting compound which probably is a tetracyclic diketone. For comparison with this substance, a further characterization was made of 2,6-dimethyl-1,2-naphthoquinone-2,3-dimethylbutadiene.

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[7] By Mrs. G. M. Wellwood.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.

RECEIVED MARCH 27, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Application of the Diene Synthesis to Halogenated 1,2- and 3,4-Phenanthrenequinones

BY LOUIS F. FIESER AND J. T. DUNN

Having found that the 3-halo derivatives of β-naphthoquinone react smoothly with dienes and afford products which can be converted easily into 9,10-phenanthrenequinones,[1] we investigated the possibility of utilizing corresponding ortho quinones derived from phenanthrene for the synthesis of compounds of the chrysene and 3,4-benzphenanthrene series.

A suitable starting material derived from 3,4-phenanthrenequinone[2] (I) was obtained very satisfactorily by a process of bromination analogous to that developed by Zincke[3] for the preparation of 3-bromo-1,2-naphthoquinone. Treated with bromine in acetic acid solution, the quinone forms a yellow dibromide from which hydrogen bromide is eliminated by the action of boiling water. That the resulting crimson-red product has the structure of 2-bromo-3,4-phenanthrenequinone is established by the following observations. The Thiele reaction proceeds without disturbance of the halogen atoms and on hydrolysis of the triacetate (V) and oxidation there is obtained a compound having the properties of an hydroxy-*p*-quinone (VI). The bromine atom therefore cannot be located at position 4. Only one other position is available in the quinonoid nucleus, and the behavior of the bromo-3-hydroxy-1,4-phenanthrenequinone under the conditions of a Fischer esterification reaction indicates that the substituent is indeed located at the position (2) in question. Whereas the unsubstituted hydroxyquinone is converted rapidly by the action of meth-

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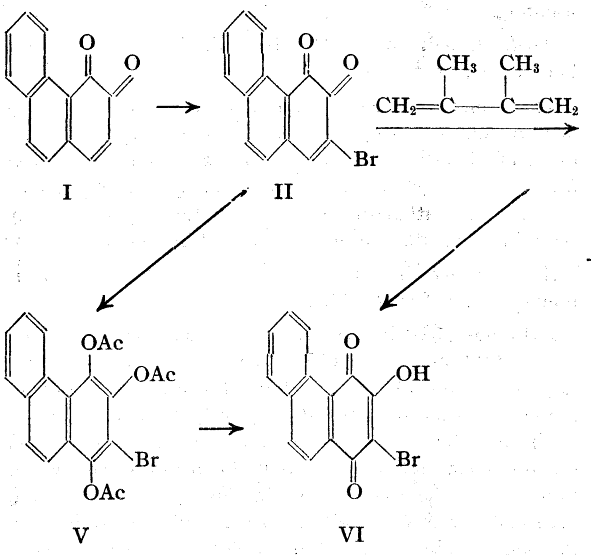
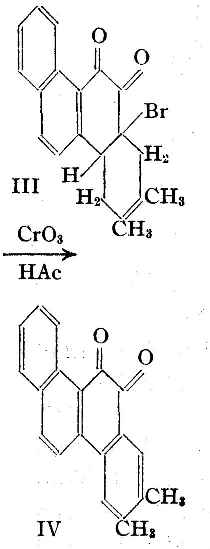
[1] Fieser and Dunn, THIS JOURNAL, **59**, 1016 (1937).

[2] Fieser, *ibid.*, **51**, 940 (1929).

[3] Zincke and Schmidt, *Ber.*, **27**, 733 (1894).

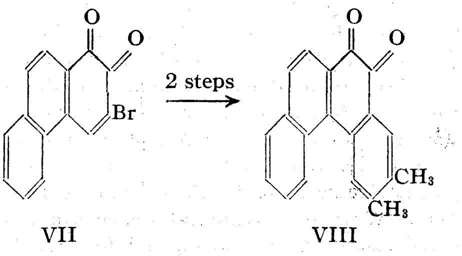
anol–hydrogen chloride into the ether,[2] the bromo compound is unaffected on prolonged boiling with the reagent. As with 2-hydroxy-3-bromo-1,4-naphthoquinone,[4] the failure of the reaction is attributable to the blocking influence of a substituent adjacent to the hydroxyl group. Another difference for which the substituent probably is responsible is that the bromo compound, unlike the parent hydroxyquinone, is not subject to ready cleavage by alkalies.





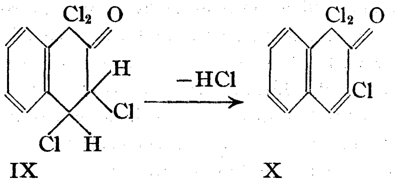
The presence of the bromine atom in the quinonoid ring is shown also by its ready elimination from the addition product (III) of 2-bromo-3,4-phenanthrenequinone and 2,3-dimethylbutadiene. The reaction between these components proceeded smoothly in chloroform solution at 100° (two hours), and the addition product, collected as an oil and not purified, was converted by the action of chromic acid into pure 8,9-dimethyl-5,6-chrysenequinone (IV) in 90% over-all yield.

1,2-Phenanthrenequinone[5] was submitted to the same series of reactions with similar results, the 3-bromo derivative VII being converted through the dimethylbutadiene addition product into 6,7-dimethyl-3,4-benz-9,10-phenanthrenequinone (VIII) in 79% yield. Using butadiene, which reacted somewhat more slowly than its dimethyl derivative, the known 3,4-benz-9,10-phenanthrenequinone[6] was obtained in satisfactory yield.



The advantage of using bromo derivatives in the diene synthesis of polynuclear compounds from ortho quinones was further demonstrated by the results of experiments with 1,2-phenanthrenequinone itself. Since this quinone is considerably more stable than β-naphthoquinone and can be obtained in a high state of purity, it seemed particularly suitable for use in the Diels–Alder reaction. A reaction with dimethylbutadiene was indeed found to occur, and the crude product was converted successfully into 6,7-dimethyl-3,4-benz-9,10-phenanthrenequinone (VIII). The addition, however, proceeded much more slowly than with the 3-bromo derivative, and considerable decomposition occurred during the long period of heating (forty-eight hours). The yield of the quinone VIII (29%) was less than half that obtained from the bromo compound.

A shorter route to halogenated phenanthrenequinones of the type required as starting materials was investigated without success. In analogy with Zincke's[7] observations concerning the chlorination of β-naphthol, it seemed possible that 3-phenanthrol might be convertible through intermediate chloro ketones similar to IX and X into 2-chloro-3,4-phenanthrenequinone. The phenanthrol, however, is attacked not only in the hydroxylated ring but also at some other part of the molecule, probably at the reactive 9,10-double bond. On conducting the chlorination in glacial acetic acid solution at a low temperature, the chief product isolated in a crystalline condition



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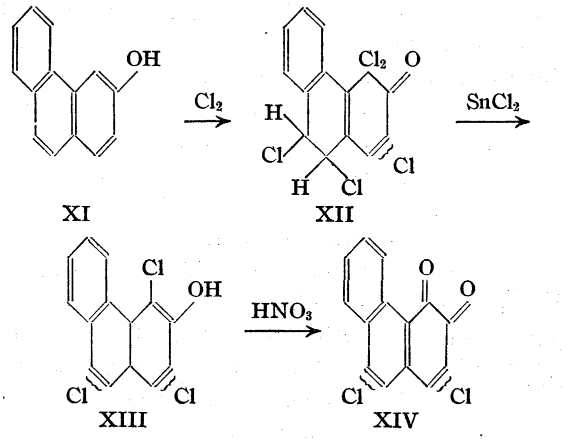
(4) Fieser, This Journal, **48**, 2922 (1926).

(5) Fieser, *ibid.*, **51**, 1896 (1929).

(6) Cook, *J. Chem. Soc.*, 2524 (1931).

(7) Zincke and Kegel, *Ber.*, **21**, 3378, 3540 (1888).

was an orange pentachloro ketone. This substance corresponds in properties to Zincke's unsaturated trichloro ketone X except for the presence of an additional pair of chlorine atoms, and the compound probably has the structure XII. Reduction with stannous chloride gave a trichlorophenanthrol (XIII), hydrogen chloride evidently being eliminated from the central nucleus simultaneously with a change in the terminal ring comparable with that observed by Zincke in the naphthalene series. The trichlorophenanthrol yielded on oxidation with nitric acid a dichlorophenanthrenequinone of the probable structure XIV. Acetic anhydride–sulfuric acid adds slowly to the quinone to give a colorless triacetate, and one halogen atom is displaced in the process. The chlorine atom in the quinonoid ring therefore is probably located at the 1-position.



Experimental Part[8]

3,4-Phenanthrenequinone Series

2 - Bromo - 3,4 - phenanthrenequinone.—A solution of 2.25 g. of 3,4-phenanthrenequinone[2] (conveniently purified by one crystallization from acetone–water, using Norite) in 235 cc. of glacial acetic acid was treated at room temperature with 1.9 g. of bromine in 40 cc. of the same solvent. The red solution turned yellow at once. (With more concentrated solutions the yellow addition product crystallized and was not easily redissolved without decomposition.) After fifteen minutes the yellow solution was stirred quickly into 410 cc. of vigorously boiling water and the resulting deep red solution was allowed to stand without disturbance. Within less than one minute the bromoquinone began to separate in long, glistening, deep crimson-red needles. The average yield of product, m. p. 211–212°, was 2.3 g. (77%). The quinone crystallizes well from glacial acetic acid, dioxane, chloroform, or benzene, in which solvents it is moderately soluble; it is sparingly soluble in alcohol or ether. The recrystallized material melted at 212–213°.

Anal. Calcd. for $C_{14}H_7O_2Br$: C, 58.54; H, 2.46. Found: C, 58.36; H, 2.75.

2-Bromo-3,4-dihydroxyphenanthrene.—A suspension of 1.1 g. of the quinone in 15 cc. of alcohol and 20 cc. of water was treated with sulfur dioxide until the solid had dissolved to a pale red solution; this was warmed slightly until pale yellow and diluted with water until crystallization commenced. The hydroquinone separated as glistening, almost colorless needles (1 g.). It is very soluble in alcohol, ether, or benzene, and moderately soluble in chloroform. A sample crystallized from the latter solvent formed colorless needles, m. p. 164–165.5°, which darkened on standing.

Anal. Calcd. for $C_{14}H_9O_2Br$: C, 58.13; H, 3.14. Found: C, 57.79; H, 3.52.

The dimethyl ether, prepared by treatment with dimethyl sulfate and potassium hydroxide in an atmosphere of nitrogen, extracted with ether, and crystallized from methanol (slow), was obtained in 98% yield as colorless, transparent prisms melting at 79–80°, and further crystallizations did not change the melting point.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.43; H, 4.13. Found: C, 60.21; H, 4.36.

2-Bromo-1,3,4-triacetoxyphenanthrene.—A suspension of 1 g. of 2-bromo-3,4-phenanthrenequinone in a cold solution of 12 drops of concentrated sulfuric acid in 10 cc. of acetic anhydride was stirred frequently at room temperature; after four to five hours a nearly colorless solution was obtained, and this was treated cautiously with water to hydrolyze the excess anhydride, using 10 cc. in all and eventually bringing precipitated material into solution at the boiling point. The filtered solution deposited nearly pure material which, after recrystallization from acetic acid, formed very fine, colorless needles, m. p. 195–196°; yield, 1.4 g. (93%).

Anal. Calcd. for $C_{20}H_{15}O_6Br$: C, 55.68; H, 3.51. Found: C, 55.91; H, 3.36.

2 - Bromo - 3 - hydroxy - 1,4 - phenanthrenequinone.—The triacetate (0.8 g.) was warmed with 10% sodium hydroxide (15 cc.) and a little alcohol until dissolved. Air was passed through the solution until the solution was dark red and showed no further change. Water (150 cc.) was added to dissolve some crystalline salt at the boiling point, and the solution was acidified. The orange-yellow precipitate when crystallized from methanol (moderately soluble), formed glistening, orange-red needles, m. p. 198–199°; yield, 0.5 g. (89%).

Anal. Calcd. for $C_{14}H_7O_3Br$: C, 55.45; H, 2.33. Found: C, 55.37; H, 2.37.

The bromohydroxyquinone (58 mg.) was recovered unchanged (50 mg.) after a solution of the substance in methanol had been refluxed for five hours. Under identical conditions, a solution of 3-hydroxy-1,4-phenanthrenequinone (56 mg.) began to deposit crystals of the ether in two minutes and after refluxing for ten minutes the ether[2] was collected and recrystallized; yield, 49 mg. (84%); m. p. 170–171°. Whereas 3-hydroxy-1,4-phenanthrenequinone is cleaved completely by boiling, dilute alkali in about four hours,[2] the 2-bromo derivative (0.4 g.) was largely recovered unchanged (0.35 g.) after being boiled for fifteen

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[8] The melting points are uncorrected. Analyses marked with an asterisk were performed by Mrs. G. M. Wellwood.

hours with 150 cc. of water containing 2.9 cc. of 10% sodium hydroxide solution.

8,9-Dimethyl-5,6-chrysenequinone (IV).—A solution of 0.5 g. of 2-bromo-3,4-phenanthrenequinone and 2 cc. of 2,3-dimethylbutadiene in 20 cc. of pure chloroform was heated at 100° for two hours, when the color had faded from red to yellow. The reddish-yellow oil remaining after removing the solvent was treated in 3 cc. of glacial acetic acid with 1 g. of chromic anhydride in 10 cc. of 80% acetic acid with gentle warming. By gradually adding water to the red solution and scratching, the reaction product was caused to separate in a microcrystalline condition; yield, 0.45 g. (90%). Recrystallized from glacial acetic acid, the quinone formed bright orange-red blades having a golden reflex, m. p. 250–251°.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.89; H, 4.93. Found: C, 83.74; H, 4.96.

1,2-Phenanthrenequinone Series

3-Bromo-1,2-phenanthrenequinone.—A fine suspension of 3.8 g. of 1,2-phenanthrenequinone (as prepared[5]) in 180 cc. of glacial acetic acid at 25° was treated with 3.3 g. of bromine in 20 cc. of this solvent, and after stirring for twenty minutes the material had dissolved. The yellow-red solution, filtered from a small amount of black material, was poured into 290 cc. of vigorously boiling water. The bromoquinone began to crystallize at once and, after cooling, it was collected and recrystallized from chloroform. It formed glistening, very dark crimson-red needles, m. p. 245–246°; yield, 3.6 g. (68%). The substance is darker in color than the isomer, and considerably less soluble in all solvents.

*Anal.** Calcd. for $C_{14}H_7O_2Br$: C, 58.54; H, 2.46. Found: C, 58.65; H, 2.83.

3-Bromo-1,2-dihydroxyphenanthrene.—A solution of 1 g. of the quinone in 20 cc. of hot dioxane was diluted with 15 cc. of water and sulfur dioxide was passed into the resulting fine suspension. After the quinone had dissolved, the solution was heated to boiling, diluted with water, and allowed to stand. On cooling, the hydroquinone separated as long, slender, colorless needles (0.9 g.). A sample recrystallized from chloroform melted at 195–196°.

*Anal.** Calcd. for $C_{14}H_9O_2Br$: C, 58.13; H, 3.14. Found: C, 58.20; H, 3.11.

The dimethyl ether, prepared as described for the isomer, crystallized from methanol as thin, elongated, transparent plates, m. p. 82–83°.

*Anal.** Calcd. for $C_{16}H_{13}O_2Br$: C, 60.43; H, 4.13. Found: C, 60.36; H, 3.92.

3 - Bromo - 1,2,4 - triacetoxyphenanthrene, obtained as above in nearly theoretical yield, formed fine, colorless needles, m. p. 188–189°, from glacial acetic acid.

*Anal.** Calcd. for $C_{20}H_{15}O_6Br$: C, 55.68; H, 3.51. Found: C, 55.62; H, 3.75.

Hydrolysis of the triacetate and air oxidation as above gave a hydroxyquinone which forms very dark red needles, m. p. 222° dec., from alcohol; analytical results were variable and undecisive.

6,7 - Dimethyl - 3,4 - benzphenanthrenequinone (VIII).—The quinone (1 g.) and diene (6 cc.) were heated in chloroform (70 cc.) for three hours and the addition product was oxidized as above; yield of crystalline product, 79%. Recrystallized from alcohol, the compound formed lustrous, fiery red plates, m. p. 194–195°.

*Anal.** Calcd. for $C_{20}H_{14}O_2$: C, 83.89; H, 4.93. Found: C, 83.63; H, 5.01.

This quinone, identified by mixed melting point determination, was obtained also on heating 1,2-phenanthrenequinone (0.5 g.), dimethylbutadiene (2 cc.) and chloroform (20 cc.) for forty-eight hours and oxidizing the crude product as above; yield, 0.2 g. (29%). The diene addition occurred only slowly, for the initially clear red solution faded only slightly during the first few hours of heating; after a time the solution began to grow steadily darker, indicating decomposition.

3,4-Benzphenanthrenequinone, prepared in the usual way from 1 g. of bromoquinone and 4 cc. of butadiene, heated in 40 cc. of chloroform for five hours, was obtained in a satisfactory condition in yield of 0.6 g. (65%). It crystallized from alcohol as bright red blades, m. p. 190–191°. Cook[6] reports the melting point 187–188° for material prepared by the oxidation of 3,4-benzphenanthrene. Attempts to convert the above substance (100 mg.) into the hydrocarbon by zinc dust distillation were unsuccessful. Reductive acetylation of 100 mg. of the quinone by the usual method gave 115 mg. of the pure **hydroquinone diacetate,** which forms small, colorless needles from dilute alcohol and melts at 194–195°.

*Anal.** Calcd. for $C_{22}H_{16}O_4$: C, 76.72; H, 4.69. Found: C, 76.38; H, 4.77.

Chlorination of 3-Phenanthrol

Pentachloro Ketone XII, Probably 1,4,4-Trichloro-3-keto - 3,4 - dihydrophenanthrene - 9,10 - dichloride.—Excess chlorine was passed at a moderate rate into a solution of 5 g. of 3-phenanthrol in 50 cc. of glacial acetic acid at 13–17°, and after standing for a few minutes the greenish-yellow solution was poured slowly into 500 cc. of cold water. The flocculent yellow precipitate which separated was washed by decantation, collected on a suction funnel, and washed thoroughly with water. The rather sticky, yellow-orange product was triturated with glacial acetic acid, which dissolved the gummy material, and on collecting the residue and washing it thoroughly with fresh solvent a clean, orange-yellow powder was obtained. The yield of this material, m. p. 175–180° dec., was 2.9 g. (30%). A sample recrystallized from glacial acetic acid (with little heating) formed thick, orange needles, m. p. 182–185°, dec.

*Anal.** Calcd. for $C_{14}H_7OCl_5$: Cl, 48.14. Found: Cl, 47.82; 47.77.

The compound is not attacked by 10% aqueous sodium carbonate solution in the cold, and extensive decomposition occurs when the mixture is heated. The chloro compound gives a dark red anilide on reaction with aniline in benzene solution. In one experiment a small amount of another chlorination product separated slowly from the initial acetic acid mother liquor in the form of colorless prisms (m. p. 191° dec.) but when this material was collected and dried it turned yellow within a few hours.

1(?),4,9(or 10)-Trichloro-3-phenanthrol (XIII).—A solution of 0.9 g. of the above compound in 18 cc. of glacial acetic acid was treated at room temperature with a concentrated solution of stannous chloride in dilute acetic acid, added by drops until a test portion of the solution gave with water a precipitate which dissolved completely in dilute alkali. On gradual dilution with water the solution deposited colorless needles of the reduction product (0.7 g., 96%). The phenanthrol formed long needles, m. p. 130–131°, from dilute alcohol.

*Anal.** Calcd. for $C_{14}H_7OCl_3$: Cl, 35.78. Found: Cl, 35.74.

The acetate crystallized from alcohol as lustrous plates, m. p. 164–165°.

*Anal.** Calcd. for $C_{16}H_9O_2Cl_3$: Cl, 31.35. Found: Cl, 31.15.

1(?),9(or 10)-Dichloro-3,4-phenanthrenequinone (XIV).—A solution of 0.35 g. of the trichlorophenanthrol in 8 cc. of glacial acetic acid was oxidized with 3 cc. of concentrated nitric acid added all at once. The solution became red immediately and then began to darken; after three to four minutes it was gradually diluted with an equal volume of water, thus precipitating the quinone in a microcrystalline condition. Recrystallization from glacial acetic acid gave small, dark red needles melting at 239–240° dec.; yield, 0.22 g. (67%).

Anal. Calcd. for $C_{14}H_6O_2Cl_2$: C, 60.65; H, 2.18. Found: C, 60.53; H, 2.53.

1(?),3,4 - Triacetoxy - 9(or 10) - chlorophenanthrene.—A suspension of 90 mg. of the quinone XIV in 6 cc. of acetic anhydride containing 6 drops of concentrated sulfuric acid was shaken at intervals and frequently warmed on the steam-bath. The material dissolved in about six hours, and after standing overnight the red-yellow solution was treated with water. One crystallization from acetic acid gave 70 mg. of yellowish rods, and after further crystallizations from alcohol the compound was obtained as slender, colorless needles, m. p. 230–231°.

*Anal.** Calcd. for $C_{20}H_{15}O_6Cl$: Cl, 9.17. Found: Cl, 9.65.

Summary

3-Bromo-1,2-phenanthrenequinone and 2-bromo-3,4-phenanthrenequinone add dienes readily and the addition products can be converted in good yield into 3,4-benzphenanthrenequinones and chrysenequinones, respectively.

From a preliminary study of the chlorination of 3-phenanthrol it appears that the substance not only is attacked in the hydroxylated ring but adds chlorine at the 9,10-position.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

10-Substituted 1,2-Benzanthracene Derivatives

BY LOUIS F. FIESER AND E. B. HERSHBERG[1]

The observation that 10-methyl-1,2-benzanthracene[2] is a potent carcinogenic agent comparable with cholanthrene and methylcholanthrene in the rapidity and regularity with which it produces tumors in experimental animals[3] has made it a matter of considerable interest to investigate additional 10-substituted derivatives of the tetracyclic hydrocarbon. The 10-methyl derivative contrasts strikingly with 1,2-benzanthracene itself, for in experiments conducted at the Royal Cancer Hospital the latter hydrocarbon has produced only one tumor (papilloma) in eighty mice tested.[4] Since compounds of more complex structure than the methyl derivative, namely, the 10-isopropyl and 10-benzyl compounds, have been tested by the English investigators[4] with entirely negative results, it is important to determine whether 10-methyl-1,2-benz anthracene occupies a unique position or is one of a possibly limited series of homologs possessing some carcinogenic activity. A series of closely related hydrocarbons of graduated potency would offer many interesting possibilities for biological and chemical experimentation.

None of the synthetic methods hitherto employed for the preparation of 10-alkyl-1,2-benzanthracenes seemed adequate for the purpose at hand without some modification. The synthesis of Fieser and Newman[2] provides a quite satisfactory, if somewhat lengthy, route to the 10-methyl compound, but it suffers from the limitation that considerable reduction occurs as a side reaction in the condensation of higher alkylmagnesium halides with 2-*o*-toluyl-1-naphthoic acid. Cook[5] obtained the 10-benzyl compound in small yield by the action of benzyl chloride on 1,2-benzanthracene in the presence of zinc dust, but direct alkylation clearly is out of the question as a general method. A third synthesis,

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[1] Lilly Research Fellow.

[2] Fieser and Newman, THIS JOURNAL, **58**, 2376 (1936).

[3] Fieser and Hershberg, *ibid.*, **59**, 394 (1937); L. F. Fieser, M. Fieser, Hershberg, Newman, Seligman and Shear, *Am. J. Cancer*, **29**, 260 (1937).

[4] Barry, Cook, Haslewood, Hewett, Hieger and Mayneord, *Proc. Roy. Soc.* (London), **B117**, 318 (1935).

briefly investigated by Cook[5,6] with only moderate success, consists in the addition of a Grignard reagent to 1,2-benz-10-anthrone (IV, below) and the dehydration of the resulting dihydroanthranol. Cook prepared 10-benzyl-[5] and 10-isopropyl-1,2-benzanthracene[6] in unspecified yield by this method. Recently, Cook, Mrs. Robinson and Goulden[5a] have overcome earlier difficulties[5] and succeeded in preparing the 10-methyl compound in the same way. The 1,2-benz-10-anthrone used in these experiments was a crude product prepared[5] by heating 2-(α-naphthylmethyl)-benzoic acid with anhydrous zinc chloride at 180°. The material was found to be so unstable that purification was not feasible.

It seemed likely that the anthrone synthesis of Cook would be capable of wide application if the anthrone were available in a more satisfactory condition, and we consequently investigated this phase of the problem. The preparation of the 2-(α-naphthylmethyl)-benzoic acid required as starting material by the reduction of 2-(α-naphthoyl)-benzoic acid with zinc dust and alkali[7] has been tried repeatedly in this Laboratory with disappointing results. Although with closely analogous keto acids reduction by this method usually proceeds very well, a product of satisfactory purity is obtained with the specific example at hand only after a tedious process of purification and in poor yield. A much better method was found in the high-pressure hydrogenation of the keto acid without solvent at 175° in the presence of copper chromite catalyst,[8] a pure product being obtained in excellent yield after a single crystallization. No reduction occurred when solvent alcohol was employed. The 2-(α-naphthoyl)-benzoic acid was at first prepared by the Friedel and Crafts reaction, but the separation of the desired product from the β-isomer[9] proved to be so tedious and wasteful that this was abandoned in favor of the Grignard condensation between phthalic anhydride and α-bromonaphthalene,[10] which was found very satisfactory. On one occasion, when commercial α-bromonaphthalene was used without further purification, the keto acid obtained had the correct melting point but failed to undergo hydrogenation even after repeated crystallization. The difficulty was traced to the reduction of the catalyst to the metallic condition under the influence of a trace of hydrogen bromide liberated from a small amount of bromonaphthoylbenzoic acid present in the material prepared from halide contaminated with dibromonaphthalene.

Cook[5] noted that sulfuric acid alone is not a satisfactory reagent for effecting the cyclization of 2-(α-naphthylmethyl)-benzoic acid since it leads to considerable oxidation and sulfonation. We found that these side reactions can be avoided to some extent by using a suitable diluent. Employing for the ring closure a mixture of sulfuric and phosphoric acids at room temperature, the crude anthrone was obtained in over 90% yield. This material, however, deteriorated badly on standing and extensive decomposition occurred on attempted crystallization. Submitted to reaction with methylmagnesium iodide or ethylmagnesium bromide, the crude products gave, after dehydration, some of the expected 10-methyl- and 10-ethyl-1,2-benzanthracene, but the yields were low and considerable unreacted material was recovered. This recovered product is quite easily purified and considerably less subject to decomposition than the starting material.

The pure, crystalline substance isolated in this way was found to be the enolic form of the compound, 1,2-benz-10-anthranol (III). It was subsequently established that the anthranol is not produced under the influence of the Grignard reagent but is present to a considerable extent in the crude product of cyclization and that addition occurs only to such of the keto-form as is contained in the material submitted to reaction. The stability in solvents of the recovered anthranol in contrast to the crude starting material suggested that a purification of the latter might be accomplished most effectively through some other functional derivative of the anthranol, such as the acetate. We were not able to prepare 1,2-benzanthranyl-10-acetate (II) satisfactorily from the very sensitive anthrone–anthranol mixture resulting from cyclization with sulfuric–phosphoric acid, but found that some of this substance is produced, along with some 1,2-benz-10-anthrone (IV), when the acid I is warmed with a mixture of sulfuric and acetic acids. It seemed likely that under conditions more favorable to acetylation

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[5] Cook, *J. Chem. Soc.*, 1087 (1930).

[5a] Cook, Robinson and Goulden, *ibid.*, 393 (1937).

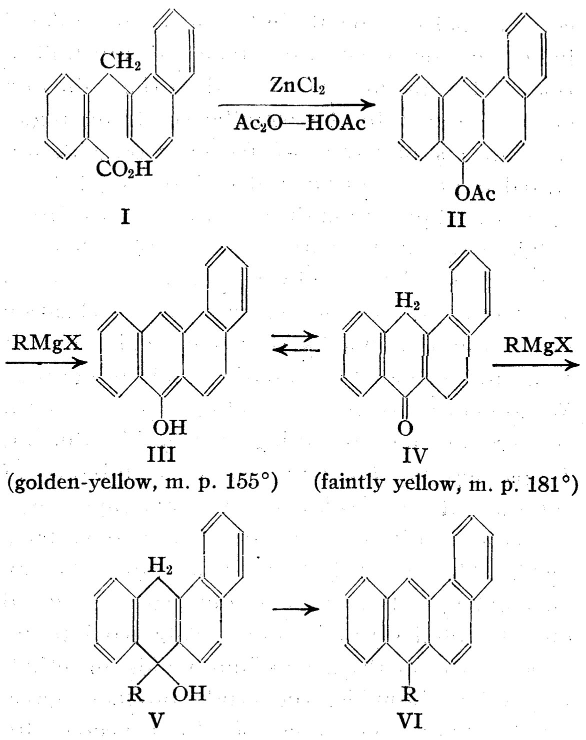
[6] Cook, *ibid.*, 456 (1932).

[7] Scholl, Seer and A. Zincke, *Monatsh.*, **41**, 583 (1920).

[8] Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

[9] Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 1420 (1920).

[10] Weizmann, E. Bergmann and F. Bergmann, *J. Chem. Soc.*, 1367 (1935).



I II

III (golden-yellow, m. p. 155°)

IV (faintly yellow, m. p. 181°)

V VI

the tautomeric equilibrium would be displaced by the removal of the anthranol as the acetate, and various mixtures containing acetic anhydride were tried. Since zinc chloride in the molten state effects ring closure,[5] we investigated the action of this substance in solution and eventually developed a method of cyclization which leaves little to be desired.

The new method consists in heating 2-(α-naphthylmethyl)-benzoic acid (I) with about 0.1 molecular equivalent of zinc chloride in a mixture of acetic anhydride and acetic acid at the boiling point for about one hour. After adding water and cooling, 1,2-benzanthranyl-10-acetate separates in a crystalline and completely pure condition in yield of about 90%. Zinc chloride in catalytic amounts also promotes cyclization in acetic anhydride solution alone, but the anhydride itself is attacked under these conditions with consequent darkening. This effect is eliminated by using some acetic acid as a diluent. Stannous chloride can be used also as the catalyst, but it does not seem to offer any advantages. The method of cyclization has been found applicable to some, if not all, other 2-arylmethyl-benzoic acids, γ-arylbutyric acids, and β-arylpropionic acids thus far investigated; a study of additional examples is under way and will be reported separately.

The hydrolysis of the acetate II was accomplished very satisfactorily by treatment with excess Grignard reagent, the pure enolic tautomer III being obtained in over 80% yield. 1,2-Benz-10-anthranol forms bright golden yellow blades melting at 155°. The substance is completely stable in the solid state and it undergoes only very slow isomerization in most solvents. Acetone combines rapidly with the anthranol to give what appears to be a labile, colorless molecular compound and in the boiling solvent the enol form partially isomerizes at a moderately rapid rate to 1,2-benz-10-anthrone (IV), which was isolated in a pure condition by crystallization from acetone–ligroin after boiling the solution to effect a partial equilibration. This process could not be carried to completion, however, for solutions containing acetone suffer decomposition after refluxing for a few hours, apparently before equilibrium is established. The anthrone IV is a faintly yellow substance melting at 181°, and it is more soluble in hydrocarbon solvents than the anthranol III. Both tautomers can be crystallized without change from benzene or toluene if the heating is not prolonged, but when a toluene solution of the anthranol is refluxed for several hours partial isomerization to the anthrone occurs. Little decomposition takes place in hydrocarbon solvents, and this was the most satisfactory method found for obtaining the anthrone in a condition suitable for the Grignard reaction.

For the preparation of the methyl ether of 1,2-benz-10-anthranol, the usual process of methylation in alkaline solution did not appear practical because in such a medium the substance is rapidly oxidized by the air to the corresponding quinone. It was found that the ether can be obtained conveniently by cleaving the acetate II with a Grignard reagent and heating the resulting solution of the magnesium bromide salt with dimethyl sulfate.

From such general comparisons as can be made with K. H. Meyer's observations concerning the parent pair of tautomers, anthranol and anthrone,[11] it appears that the enol form is a somewhat more favored structure in the 1,2-benzanthracene series than with the anthracene compounds, as would be expected from theoretical considerations,[12] but until a direct comparison of

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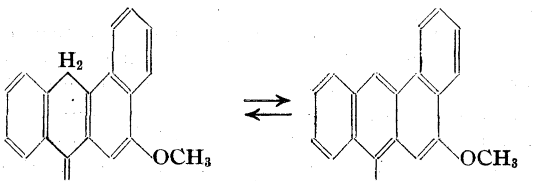
[11] K. H. Meyer, *Ann.*, **379**, 37 (1911); K. H. Meyer and Sander, *ibid.*, **396**, 133 (1913).

[12] Fieser and Lothrop, THIS JOURNAL, **58**, 749 (1936).

the two systems can be made it is perhaps well to reserve judgment on this point.

Having developed a good method of preparing pure 1,2-benz-10-anthranol and a reasonably satisfactory method of effecting its isomerization, little difficulty was experienced in synthesizing a series of 10-alkyl-1,2-benzanthracenes. In some instances crystallizates consisting wholly or largely of the keto form were employed for the Grignard reaction, but the best procedure consists in refluxing a solution of the anthranol in toluene for several hours and adding the cooled solution containing a large proportion of the anthrone to a solution of the Grignard reagent. Addition of the reagent proceeds rapidly and smoothly and moderate heating of the reaction product is sufficient to effect dehydration of the dihydroanthranol derivative (V). Some 1,2-benz-10-anthranol not originally isomerized usually can be recovered with ease in a satisfactory condition and traces of oxygen-containing compounds are eliminated readily by adsorption on alumina. Pure *n*-alkyl compounds were obtained in this way in average yield of about 50%. The 10-methyl-1,2-benzanthracene obtained was identical with the material synthesized by Fieser and Newman.[2] The 10-isopropyl compound was prepared for comparison with Cook's material[6] and the properties were as reported. The yield in this preparation was poor and in one experiment the principal product isolated was a substance having the composition of a tetrahydro derivative of 10-isopropyl-1,2-benzanthracene; it yielded the latter hydrocarbon on dehydrogenation with sulfur. We plan to investigate this substance further and to study the reduction of 1,2-benzanthracene derivatives under other conditions. The more usual type of reduction, resulting in the formation of 1,2-benzanthracene, was observed to occur to an appreciable extent only in one instance. The series of 10-substituted derivatives prepared included the ethyl, *n*-propyl, *n*-butyl, *n*-amyl, and allyl compounds. 10-Allyl-1,2-benzanthracene is converted smoothly on hydrogenation into a hydrocarbon identical with the synthetic 10-*n*-propyl derivative.

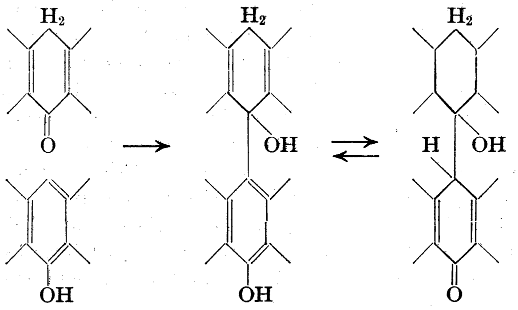
A few 10-alkyl derivatives of the weakly carcinogenic[13] 3-methoxy-1,2-benzanthracene also were prepared, and here the process proved to be considerably simpler. The pale yellow, crude product resulting from the cyclization of 2-(4′-methoxy-1′-naphthylmethyl)-benzoic acid with cold sulfuric acid,[14] although tending to decompose on attempted crystallization from most solvents,[14] is less sensitive than the methoxyl-free material.



VII (faintly yellow, m. p. 184°)

VIII (deep brown, m. p. 193°)

In each case cyclization with sulfuric acid seems to produce initially the keto form, which isomerizes to some extent when washed with water and undergoes slow change even on storage in the solid state. It was found that pure 3-methoxy-1,2-benz-10-anthrone (VII) can be obtained easily in fair yield by quickly crystallizing the crude, moist cyclization product from acetone. The anthranol, VIII, was first isolated in small amount from the mother liquor, and this tautomer later was prepared by the isomerization of the pure anthrone with boiling pyridine. There was isolated as a by-product in this reaction a high-melting, sparingly soluble, yellow compound having the composition of the starting material. This most likely is formed by the condensation of the enol and keto forms, giving the dianthranol-like substance IXa or the tautomer IXb. A similar substance was isolated as a by-product in the preparation of 10-*n*-amyl-1,2-benzanthracene and, since it is colorless, it probably has the ketonic structure IXb.



IXa IXb

From the pure anthrone VII, the 10-methyl, 10-ethyl, and 10-*n*-propyl derivatives of 3-methoxy-1,2-benzanthracene were obtained in good yield by the Grignard synthesis.

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[13] Fieser, Hershberg, Long, Jr., and Newman, THIS JOURNAL, **59**, 475 (1937).

[14] Fieser and Dietz, *ibid.*, **51**, 3141 (1929).

The 1,2-benzanthracene derivatives described in this paper are being tested for carcinogenic activity by Dr. M. J. Shear. The synthesis of 10-substituted compounds is being continued.

Experimental Part[15]

2-(α-Naphthoyl)-benzoic Acid.—Material prepared by the Friedel and Crafts reaction in tetrachloroethane solution at 10° and obtained in 84% yield after one crystallization, melted at 150–170° and afforded a pure product only after several recrystallizations and with heavy losses. In the large-scale preparation by the alternate method,[10] 145 g. of carefully fractionated α-bromonaphthalene, b. p. 155.0–155.5° (25 mm.), m. p. 4–5°, was converted into the Grignard reagent in benzene (100 cc.)–ether (400 cc.) solution and this was added slowly to a vigorously stirred suspension of 111 g. of phthalic anhydride in 700 cc. of hot benzene. After stirring for two hours on the steam-bath, the mixture was worked up as usual and the product, collected after removing the solvent with steam, was mixed with soda solution and submitted to steam distillation. The dinaphthyl phthalide present remained undissolved, and after treating the solution with Norite at 10–15° the acid was precipitated, washed, drained well with the use of a rubber dam, and crystallized from an alcohol (500 cc.)–water (300 cc.) mixture; yield, 144 g. (75%); m. p. 174–176°.

2-(α-Naphthylmethyl)-benzoic Acid.—Reduction with zinc and alkali[7] gave satisfactory material, m. p. 147–148°, in about 20% yield after several crystallizations from benzene–ligroin and methanol.

In a typical hydrogenation experiment 144 g. of the once crystallized, halogen-free keto acid and 8 g. of copper chromite catalyst (37 KAF[8]) were shaken with hydrogen at 2300–1500 lb. (156–102 atm.) pressure and 175° for two and one-half to three hours, when the reaction was complete. The temperature may be raised to 200° without ill effect. On cooling the bomb the product was found as a light green, crystalline cake. It was dissolved in a solution of 60 g. of sodium carbonate in 500 cc. of water by warming on the steam-bath and the solution was treated with Norite and poured into dilute hydrochloric acid. The collected and washed precipitate, crystallized while damp from 1500 cc. of methanol and 500 cc. of water, gave in the first crop 113 g. (82%) of colorless product, melting at 144–146° and suitable for cyclization. Only oily material was obtained from the mother liquor. The recrystallized acid formed flat needles, m. p. 148–148.5°.

Keto acid prepared by the Friedel and Crafts synthesis also was hydrogenated easily; with repeatedly recrystallized acid prepared from Eastman α-bromonaphthalene, b. p. 146–149° (16 mm.), the catalyst invariably was reduced to the metallic condition and the keto acid was recovered unchanged.

Cyclization of 2-(α-Naphthylmethyl)-benzoic Acid (I). (a) With Sulfuric–Phosphoric Acid.—The finely powdered (ball mill) acid (25 g.) was added to a vigorously stirred mixture of 200 cc. of concentrated sulfuric acid and 400 cc. of sirupy phosphoric acid (85%) at 20–30° and after two and one-half hours the deep red solution was filtered through sintered glass to remove unchanged acid (3.3 g.) and poured on cracked ice. The collected pale yellow precipitate was washed well with water and with dilute hydrochloric acid and dried in vacuum at room temperature; yield, 19.5 g. (94%); m. p. 130–135°.

This material deteriorates rapidly on standing; it is considerably less stable when washed with dilute soda solution, for this seems to promote isomerization to the enol form and secondary changes. Some isomerization probably occurs during the process of drying. Solutions of the acid-washed product darken rapidly, and attempted crystallizations were unsuccessful. In a typical Grignard reaction with freshly prepared material, 12 g. of the crude anthrone–anthranol mixture gave 2.25 g. of hydrocarbon and 5.5 g. of recovered 1,2-benz-10-anthranol, indicating the presence of at least 20% of keto form and 50% of enol form in the mixture.

(b) **With Sulfuric–Acetic Acid.**—A solution of 6 g. of the acid (I) in 70 cc. of glacial acetic acid was added to 90 cc. of concentrated sulfuric acid diluted with 20 cc. of glacial acetic acid, and after maintaining the mixture at 50–60° for twenty minutes it was poured on ice. The collected solid, washed with acetone and crystallized from this solvent, gave 2.3 g. of 1,2-benzanthranyl-10-acetate, m. p. 152–154°, together with some 1,2-benz-10-anthrone.

(c) **With Zinc Chloride as Catalyst.**—The most satisfactory procedure found was as follows. A mixture of 5 g. of 2-(α-naphthylmethyl)-benzoic acid, 30 cc. of glacial acetic acid, 20 cc. of acetic anhydride, and 0.4 g. of anhydrous zinc chloride was refluxed for one hour, during which time the solution acquired only a pale yellow color. Water was added cautiously under reflux in amount sufficient to produce a saturated solution, and on slow cooling very pure **1,2-benzanthranyl-10-acetate (II)** separated in beautiful, colorless needles; yield, 4.95 g. (91%). The material softened at 161° and melted at 163–163.5°. Cook[5] reports that the ("straw-colored") sample prepared by acetylation of the crude anthrone melted at 156° to a cloudy liquid becoming clear at 163°.

In earlier experiments, using as much as 75 g. of the acid I, the acetate was obtained in a slightly less pure condition in 70–80% yield on heating the acid for about one hour in acetic anhydride containing catalytic amounts of zinc chloride, stannous chloride, or a mixture of these halides. Acetic anhydride itself is attacked at the boiling point by these reagents, with considerable darkening, and when the undiluted anhydride was employed for cyclization the solution invariably turned dark brown. The acetate was brown and usually melted at about 153–156°; the melting point became constant at 162.5–163° only after seven crystallizations. Dilution with acetic acid eliminated this difficulty.

1,2-Benz-10-anthranol (III).—To effect cleavage, 16.1 g. of the acetate (II) was added to the Grignard reagent from 38 g. of *n*-butyl bromide, 150 cc. of benzene was added, the ether was allowed to distil, and the clear, deep orange to brown solution was refluxed for one hour. After treatment with dilute hydrochloric acid, the benzene layer was separated while hot, and on concentrating the solution a first crop of product (10.3 g.), m. p. 152–154°, and a second crop (1.3 g.), m. p. 148–150°, were obtained (yield,

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[15] All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

84%). On recrystallization from benzene the substance separated as rosets of lustrous, golden yellow prismatic blades, m. p. 154.5–155.5°.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.49; H, 4.96. Found: C, 88.49; H, 4.85.

1,2-Benz-10-anthranol is readily soluble in glacial acetic acid or benzene and moderately soluble in alcohol; the solutions are only pale yellow in color and exhibit a blue fluorescence in ultraviolet light. The first two solvents are most satisfactory for crystallization. When the powdered anthranol is covered with a little acetone it sets to a cake, and on stirring the yellow substance rapidly changes to a colorless solid. This appears to be a labile molecular compound of the enol form, for when it was collected rapidly by centrifugation it turned yellow on drying and the melting point was that of the anthranol. The pure anthranol dissolves in dilute alkali very slowly in the cold but rapidly when warmed, yielding a yellow solution which on being shaken with air soon becomes cloudy, owing to the separation of the corresponding quinone (vat test).

1,2-Benz-10-anthranol was obtained also by refluxing the acetate (1 g.) with methanol (100 cc.) saturated with hydrogen chloride for fifteen hours. The product was precipitated with water and crystallized from benzene–ligroin, giving 0.5 g. of anthranol, m. p. 150–153°.

1,2-Benz-10-anthrone.—Isomerization of the anthranol seems to take place more rapidly in acetone than in other solvents, but secondary changes occur fairly soon in boiling acetone and considerable material is destroyed if refluxing is continued for more than a brief period. In isolated experiments the pure anthrone was obtained in about 50% yield by crystallization of the anthranol from dilute acetone, but the results were irregular and the material in the mother liquor was not recoverable. The keto form was isolated in yields of 20–25% by crystallization from acetone–ligroin, and by evaporating solutions of the anthranol in acetone at room temperature in vacuum.

Pure 1,2-benz-10-anthrone can be recrystallized without change from acetone or benzene and forms faintly yellow needles melting at 180–181°, dec.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.49; H, 4.96. Found: C, 88.34; H, 5.01.

The compound is insoluble in cold alkali but dissolves fairly readily on boiling to a yellow solution which soon becomes cloudy through oxidation. The anthrone is more soluble in hydrocarbon solvents than the anthranol and the solutions are colorless and non-fluorescent.

10-Methoxy-1,2-benzanthracene.—To the Grignard reagent from 3.84 g. of *n*-butyl bromide in ether, 2 g. of 1,2-benz-10-anthranyl acetate was added. After refluxing for one hour, 7.1 g. of dimethyl sulfate was added in 50 cc. of toluene and the mixture was heated for four hours on the steam-bath, allowing the ether to distil. Water was added, the mixture was warmed and stirred for one hour on the steam-bath to decompose the excess reagent, and the washed toluene layer was diluted with benzene and passed through a tower of activated alumina, which removed some unmethylated anthranol. The filtrate was evaporated to dryness and the residue crystallized from benzene–ligroin, giving 1.0 g. (55%) of satisfactory material, m. p. 108–110°. The recrystallized ether formed colorless, diamond-shaped prisms, m. p. 110.5–111°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.35; H, 5.47. Found: C, 88.19; H, 5.72.

10-Alkyl-1,2-benzanthracenes

In the most satisfactory procedure, a solution of pure 1,2-benz-10-anthranol in toluene was refluxed for twelve hours to effect partial isomerization and allowed to cool; the solution was decanted from crystals of anthranol which separated, this material was refluxed with fresh toluene for seven hours, and the two solutions were combined and added to the Grignard reagent. Yields of hydrocarbon up to 66% show that at least this proportion of the keto form is produced by this treatment. The keto form does not appear to suffer isomerization to any appreciable extent in the course of the reaction, for the yield of hydrocarbon (ethyl) from the pure anthrone was 82%. The Grignard reaction is rapid, and usually the mixture was decomposed after stirring and warming for about one hour on the steam-bath. The organic layer was separated and washed, and after removing the solvent by distillation the residue was heated for a few minutes on the hot-plate in order to effect the complete dehydration of the dihydroanthranol derivative (V). The material was then taken into benzene and the solution was allowed to cool. Some unchanged 1,2-benz-10-anthranol often crystallized at this point and could be recovered in a satisfactory condition. The anthranol can be separated very easily from the (very soluble) hydrocarbon present in the solution, but the recovered material was not employed for the preparation of a sample of a different hydrocarbon when this was to be used for biological experiments. This limitation does not apply to the preparation of the anthranol from its acetate, for here there is little chance of the formation of a hydrocarbon and the purification was more than adequate to remove possible traces of the very soluble *n*-butyl compound. Traces of the anthrone, anthranol, and other contaminants were removed very effectively by next passing the benzene solution through a tower of activated alumina, and the hydrocarbon was obtained in a very satisfactory condition from the filtrate.

The properties and analyses of the hydrocarbons and their picrates are given in the table. The hydrocarbons crystallize well from methanol or ethanol, as do the picrates. The hydrocarbons and their solutions show a brilliant blue fluorescence in ultraviolet light. 10-Methyl-1,2-benzanthracene, prepared only in a qualitative experiment from a crude anthrone–anthranol mixture, melted at 139–140° and gave no depression when mixed with the sample of Fieser and Newman.[2] Additional details of individual experiments are recorded below. Where fractionation of a commercial sample of an alkyl halide was required, the boiling point of the material used is recorded.

Ethyl Compound.—A solution of 1.8 g. of pure 1,2-benz-10-anthrone, m. p. 180–181°, in 100 cc. of hot benzene was added slowly to the stirred Grignard reagent from 8.1 g. of ethyl bromide in 100 cc. of ether. After a transient red phase, the solution became light greenish-yellow; refluxing was continued for three hours. The yield of once crystallized (from alcohol) hydrocarbon, m. p. 112–113°, was 1.55 g. (82%).

***n*-Propyl Compound.**—Eight grams of 1,2-benz-10-anthranol was refluxed for twelve hours with 100 cc. of toluene, the unchanged enol which crystallized on cooling was refluxed with 100 cc. of fresh toluene; the solutions were combined and added to the Grignard reagent from 3.9 g. of *n*-propyl chloride, b. p. 45.7–46.2°. On working up the mixture, 2.1 g. of 1,2-benz-10-anthranol was recovered and the first crop of *n*-propyl-1,2-benzanthracene from methanol melted at 100–102° and weighed 4.3 g. (66%, allowing for the recovery). The melting point was constant after four recrystallizations. The second crop of crystals (0.45 g.) consisted largely of 1,2-benzanthracene, which after further purification was identified by mixed melting point determination.

10-*i*-Propyl-1,2-benzanthracene and the Tetrahydro Derivative.—In the first experiment 4.5 g. of crude 1,2-benz-10-anthrone collected from several isomerization experiments was added in benzene solution to the Grignard reagent from 2 g. of magnesium and 6.5 g. of commercial isopropyl chloride (which on subsequent fractionation distilled at 34.9–35.0°). The ether was largely removed by distillation and the greenish-yellow solution was refluxed for five hours. The crude oily product crystallized only slowly; recrystallization from dilute acetic acid gave 2 g. of material, m. p. 71–73°, and 0.5 g., m. p. 69–71° (50%). On further crystallization from methanol the hydrocarbon formed iridescent, cream colored leaflets, m. p. 72.5–73.5°. The picrate separates as reddish-black, well-formed needles from methanol and melts at 134.5–135.5°. The analyses indicate that the hydrocarbon is a **10-*i*-propyltetrahydro-1,2-benzanthracene.**

Anal. Calcd. for $C_{21}H_{22}$: C, 91.91; H, 8.10. Found: C, 92.00; H, 7.95. Picrate, calcd. for $C_{21}H_{22}{\cdot}C_6H_3O_7N_3$: C, 64.41; H, 5.00; N, 8.34. Found: C, 64.67; H, 4.81; N, 8.58.

Later observations suggest that the reduction to the tetrahydro compound may have occurred at an earlier stage in the process rather than in the Grignard reaction, and this possibility is being investigated further.

When the hydrocarbon (0.5 g.) was heated with selenium at 300–305° for ten hours, the extracted product crystallized from methanol as colorless plates (0.15 g.) melting at 157–159°. The melting point was raised to 159–160° on further purification, and the substance gave no depression when mixed with an authentic sample of pure 1,2-benzanthracene melting at the same temperature. The isopropyl group at the 10-position evidently is eliminated in the course of the high-temperature dehydrogenation, but when the tetrahydro compound (0.2 g.) was heated for one-half hour with sulfur (50 mg.) at 240–245° the reaction product obtained melted at 93–93.5° and was found by mixed melting-point determination to be identical with the sample of 10-isopropyl-1,2-benzanthracene prepared as described below. The tetrahydro compound (0.2 g.), warmed in glacial acetic acid solution (5 cc.) with chromic anhydride (0.16 g.) in dilute acetic acid (2 cc.) for one and one-half hours, was converted into 1,2-benzanthraquinone (25 mg.), identified by comparison with an authentic sample.

In further experiments the Grignard reagents from redistilled isopropyl chloride (b. p. 34.9–35.0°) and from isopropyl bromide (b. p. 59.3–59.5°) were brought into reaction with crude 1,2-benz-10-anthrone under conditions very similar to those described above, but the only product isolated in a pure condition was 10-*i*-propyl-1,2-benzanthracene. In the experiment with the bromide there was obtained from 6 g. of the anthrone 2 g. of a crude hydrocarbon crystallizate melting at about 58–62°. After five crystallizations from methanol, the 10-isopropyl compound was obtained in a satisfactory condition, m. p. 93–93.5° (0.8 g.). The results were similar in the second experiment with isopropyl chloride.

Allyl Compound.—1,2-Benz-10-anthranol was isomerized with toluene as above and treated with two equivalents of allylmagnesium bromide, prepared in 80% yield according to Gilman and McGlumphy.[16] Once crystallized hydrocarbon, m. p. 117–122°, was obtained in 49% yield, and three crystallizations from ethyl alcohol gave a pure product. On hydrogenation in absolute alcoholic solution, using Adams catalyst, the allyl compound was converted into 10-*n*-propyl-1,2-benzanthracene, m. p. 106.5–107.5° (78% yield).

10-ALKYL-1,2-BENZANTHRACENES

	Hydrocarbon							Picrate			
			Analyses, %						Analyses, %	
			Carbon		Hydrogen				Nitrogen	
Alkyl group	M. p., °C.	Description	Calcd.	Found	Calcd.	Found	M. p., °C.	Description	Calcd.	Found
Ethyl	113.5–114	Faintly green-yellow needles	93.71	93.48	6.29	6.28	141–141.5	Dull red needles	8.66	8.49
n-Propyl	107–108	Colorless needles	93.30	93.01	6.70	6.97	126.5–127.5	Dull red needles	8.42	8.32
i-Propyl	93–93.5[a]	Thick, pale yellow needles	93.30	93.13	6.70	6.79	159–160[b]	Light reddish-brown needles	8.42	8.37
Allyl	125.5–126.5	Pale yellow needles	93.99	93.70	6.02	6.16	132–133	Deep red needles	8.45	8.44
n-Butyl	96.8–97.5	Silky, greenish fluorescent needles	92.89	93.04	7.11	6.95	115–115.5	Orange-red needles[c]	8.19	8.22
n-Amyl	82.5–83.5	Silky, greenish fluorescent needles	92.56	92.50	7.45	7.60	111–111.5	Dull red needles	7.97	7.95

[a] Cook[6] reports 94–95°. [b] Cook[4] reports 157–158°. [c] About a twofold excess of picric acid is required in the crystallization of the picrate to prevent its dissociation.

***n*-Butyl Compound.**—Using crude 1,2-benz-10-anthrone (3.45 g.) and *n*-butyl chloride (10.5 g.), b. p. 77.5–78.4°, the yield of crude hydrocarbon, m. p. 92–95°, was 2.25 g. (56%).

***n*-Amyl Compound.**—From 7.6 g. of the anthranol, isomerized with toluene, and 9.4 g. of *n*-amyl bromide, b. p. 127.5–128°, there was obtained 1 g. of a sparingly soluble condensation product, which crystallized from the toluene solution after concentration, and 3.4 g. (37%) of the hydrocarbon, m. p. 77–79° (a second crop of 1.2 g. (13%) melted at 65–70°). The pure hydrocarbon, obtained on three crystallizations from methanol, exhibits a brilliant bluish-green fluorescence even in daylight.

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(16) Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

The condensation product forms colorless needles from toluene and melts at 265–267°, dec. The composition is that of the anthrone and anthranol, and the properties are suggestive of a dimolecular, dianthrone-like structure (keto form of IX).

Anal. Calcd. for $C_{36}H_{24}O_2$: C, 88.49; H, 4.94. Found: C, 88.95, 88.89; H, 4.98, 5.11.

3-Methoxy-10-methyl-1,2-benzanthracenes

3-Methoxy-1,2-benz-10-anthrone (ol).—It was found expedient to conduct the cyclization of 2-(4′-methoxy-1′-naphthylmethyl)-benzoic acid (20 g.) at 3–5° rather than at 20°.[14] The pale yellow precipitated material was drained well with the use of a rubber dam and divided into three portions. Each portion, while still moist, was dissolved quickly in hot acetone and the solution was rapidly concentrated until crystals began to form. The combined first crops, consisting chiefly of the anthrone, weighed 6.6 g. (35%) and melted at 170–175°. A second combined crop of 6.2 g. consisted of a mixture of the keto and enol forms, and some brown crystals of the anthranol could be separated mechanically with little difficulty.

After three crystallizations from acetone the anthrone melted constantly at 183–184° and formed long, silky, pale yellow needles. The substance is very soluble in benzene or glacial acetic acid and moderately soluble in acetone or alcohol. It is insoluble in cold, dilute alkali and hot alkali gives a yellow oil. The **anthranol,** obtained as above and also by the action of boiling pyridine on the pure ketone, crystallizes from glacial acetic acid as fan-shaped clusters of short, deep brown prisms melting at 192–193°. The anthranol is more soluble in hydroxylic solvents and acetone than the tautomer.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.18; H, 5.15. Found (anthrone): C, 82.85; H, 5.24; (anthranol) C, 82.84; H, 5.50.

On isomerizing the anthrone with pyridine there was obtained in addition to the anthranol a sparingly soluble **condensation product** (probably IXa) which formed yellow needles from glacial acetic acid and melted with decomposition in the range 268–275°. When the capillary was inserted in a bath at 230°, the sample melted and resolidified without darkening, and melted with decomposition at 268–275°.

Anal. Calcd. for $C_{38}H_{28}O_4$: C, 83.18; H, 5.15. Found: C, 83.29; H, 5.02.

3-Methoxy-10-methyl-1,2-benzanthracene.—3-Methoxy-1,2-benz-10-anthrone (3.2 g., m. p. 179–181°) was added as a solid to the Grignard reagent from 4 g. of magnesium and methyl chloride in 150 cc. of ether, 100 cc. of benzene was added to the clear solution, the ether was distilled, and the solution was refluxed for three hours. After decomposition and separation of the layers, the benzene solution was evaporated, the residue was heated on the hot-plate to effect dehydration of the dihydroanthranol, and after passing a solution of the residue in benzene through a tower of alumina, the reaction product was obtained by concentrating the solution and adding ligroin; yield, 1.7 g. (53%); m. p. 182–183°. Recrystallization from alcohol and from benzene–ligroin gave slender, faintly yellow needles, m. p. 183–183.5°. The picrate, when prepared in alcohol–benzene, formed brown needles, m. p. 141–143°, but it changed to orange-red needles, m. p. 149–150°, when recrystallized from benzene–ligroin. The compound contains two molecules of picric acid, one probably being associated with the hydrocarbon residue and the other with the ether group.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.24; H, 6.34. Picrate, calcd. for $C_{20}H_{16}O \cdot 2C_6H_3O_7N_3$: N, 11.51. Found: N, 11.27.

3-Hydroxy-10-methyl-1,2-benzanthracene was prepared by refluxing the ether (0.5 g.) in glacial acetic acid (20 cc.) with 48% hydrobromic acid for one hour. The deep green solution deposited green needles on cooling. After recrystallizing the product twice from dilute acetic acid and once from benzene–ligroin, the hydroxy compound (0.2 g.) formed straw-colored, silky needles, m. p. 193–194°, dec. The compound is very soluble in alcohol or acetic acid and moderately soluble in benzene.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.35; H, 5.47. Found: C, 88.39; H, 5.71.

3-Methoxy-10-ethyl-1,2-benzanthracene, prepared as above, was obtained in a satisfactory condition in 67% yield. The substance crystallizes from benzene–alcohol as faintly yellow, diamond-shaped prisms, m. p. 161–161.5°. The picrate forms brick-red needles, m. p. 143.5–144°, from benzene–ligroin.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.01; H, 6.36. Found: C, 88.11; H, 6.52. Picrate, calcd. for $C_{21}H_{18}O \cdot 2C_6H_3O_7N_3$: N, 11.29. Found: N, 11.12.

3-Methoxy-10-*n*-propyl-1,2-benzanthracene.—Using *n*-propyl chloride, the yield of material, m. p. 134–135°, was 76%. After three crystallizations from benzene–alcohol, the compound formed nearly colorless needles, m. p. 136–136.5°. The picrate separated from benzene–ligroin as glistening, brick-red elongated plates, m. p. 140–140.5°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.94; H, 6.73. Found: C, 87.77; H, 6.45. Picrate, calcd. for $C_{22}H_{20}O \cdot 2C_6H_3O_7N_3$: N, 11.11. Found: N, 11.35.

Summary

The preparation of a series of 10-alkyl-1,2-benzanthracenes, of interest in connection with the correlation of carcinogenic activity and structure, presented certain difficulties largely associated with the instability of the crude 1,2-benz-10-anthrone obtained by known methods of cyclization. The difficulty was overcome by the development of a new method of cyclization, using zinc chloride as a catalyst in acetic acid–anhydride solution, and yielding the anthranol acetate. Cleavage with a Grignard reagent gave the pure anthranol, and this was partially isomerized to the anthrone with boiling toluene. By the addition of Grignard reagents to the anthrone, and dehydration, the desired hydrocarbons were easily synthesized.

10-Alkyl derivatives of 3-methoxy-1,2-benzanthracene were obtained by a similar but simpler process.

CONVERSE MEMORIAL LABORATORY
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[CONTRIBUTION FROM THE METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Heat Capacities of Selenium Crystals, Selenium Glass, and Tellurium at Low Temperatures[1]

BY C. TRAVIS ANDERSON[2]

The data presented in this report represent a portion of an investigation being carried out at the Pacific Experiment Station of the U. S. Bureau of Mines on the possible specific heat anomalies of manganese selenide, and telluride, similar to those already found in the oxide[3] and the sulfide.[4]

Since it was necessary to prepare pure selenium and tellurium to be used in this investigation, it was considered desirable to make low temperature specific heat measurements on these materials.

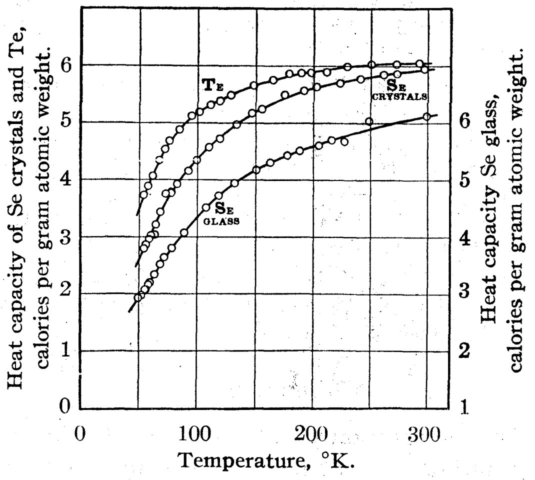

Fig. 1.—The heat capacity of selenium crystals, selenium glass and tellurium, in calories per gram atomic weight.

Materials.—The tellurium used in this investigation was furnished through the courtesy of Mr. J. O. Betterton of the American Smelting and Refining Co. The sample of selenium was of regular C. P. quality.

Both the selenium and tellurium were purified further by vacuum distillation. At temperatures slightly above their melting points, the purification of the selenium was carried out in a glass apparatus while quartz was used for the tellurium. The samples were distilled a number of times, until no residue remained in the distilling flask or condensed material accumulated above the main body of distillate.

In preparing the samples, the glassy form of selenium was usually obtained in the distillation. To convert the glass to the crystals, the selenium was alternately warmed and cooled until the mass crystallized. The only detectable impurities found to be present were approximately 0.2% tellurium in the selenium and a similar amount of selenium in the tellurium. No corrections were made for these small amounts of impurities. Measurements were made on 261.3 g. of the selenium crystals, 237.4 g. of the selenium glass, and 374.2 g. of the tellurium.

The Specific Heats.—The results obtained in this Laboratory on the heat capacities of selenium crystals, selenium glass, and tellurium, expressed in gram calories (15°) per gram atomic weight, are shown graphically in Fig. 1. The experimental values for the heat capacities are given in Tables I, II, and III. The calculations were made on the basis of Se = 78.96 and Te = 127.61.

TABLE I

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF SELENIUM CRYSTALS

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
54.4	2.786	77.7	3.772	155.4	5.236
56.1	2.864	82.8	3.920	174.5	5.494
58.7	2.956	92.4	4.149	191.5	5.562
60.1	3.018	99.5	4.342	202.7	5.633
63.4	3.035	110.0	4.566	223.2	5.702
64.6	3.211	119.3	4.724	240.9	5.776
68.3	3.428	133.9	4.974	261.2	5.850
72.9	3.746	147.0	5.166	272.7	5.861
77.6	3.773			296.5	5.952

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[3] Millar, THIS JOURNAL, **50**, 1875 (1928).

[4] Anderson, *ibid.*, **53**, 476 (1931).

TABLE II

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF SELENIUM GLASS

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
49.9	2.916	71.9	3.634	162.7	5.302
52.5	2.974	78.3	3.798	177.4	5.428
55.5	3.066	88.9	4.070	188.4	5.515
56.2	3.071	107.7	4.509	205.0	5.606
58.1	3.155	118.6	4.720	216.2	5.704
59.5	3.188	132.0	4.942	227.3	5.684
63.3	3.327	150.7	5.175	249.0	6.040
68.2	3.513			299.1	6.127

TABLE III

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF TELLURIUM

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.0	3.729	95.1	5.121	189.4	5.866
57.6	3.884	101.8	5.185	198.0	5.876
61.8	4.063	111.6	5.310	211.8	5.892
67.4	4.337	119.5	5.383	229.5	5.994
72.3	4.536	128.5	5.479	250.3	6.034
76.0	4.677	147.9	5.654	272.6	6.027
84.9	4.878	164.4	5.747	292.0	6.054
		178.4	5.859		

Calculation of Entropies

In fitting the experimental data with Debye and Einstein functions it was found desirable to plot three times the specific heat against the logarithm of the temperature. This method can best be demonstrated by use of the recent data given by Eastman and McGavock[5] for sulfur, which is a member of the same periodic group. Their measurements were extended to lower temperatures than those reported in this paper, and the heat capacity of sulfur was lower than that of either selenium or tellurium at corresponding temperatures. By plotting 3 C_p *vs.* log T, their points fall on a Debye curve up to about 30°K., while on the usual C_p *vs.* log T plot the points fall below the Debye curve above 17°K. Combinations of Debye and Einstein functions can be used to fit their experimental data accurately to above 100°K. Unless this method of extrapolating were used it would be very difficult to obtain good values for the entropies of selenium and tellurium. The extended curves coincided with Debye functions having the following parameters (Θ): selenium crystals, 74; selenium glass, 65; and tellurium, 45.

The following combinations of Debye and Einstein functions were found to fit the specific heat curves.

$$C_{\text{Se cryst.}} = \frac{1}{3}\,\mathrm{D}\left(\frac{74}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{180}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{321}{T}\right)$$

$$C_{\text{Se glass}} = \frac{1}{3}\,\mathrm{D}\left(\frac{65}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{152}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{361}{T}\right)$$

$$C_{\text{Te}} = \frac{1}{3}\,\mathrm{D}\left(\frac{45}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{142}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{206}{T}\right)$$

The results of the entropy calculations from the experimental heat capacity data as well as from the function sums are given in Table IV. The reader should note that the entropies given are the summations from 0 to 298.1°K., which are identical with $S^{\circ}_{298.1}$ for the crystalline materials, but not for the selenium glass, which presumably has zero-point entropy. Existing high temperature specific heat measurements on selenium from 298.1° to the melting point are inadequate to calculate the actual entropy of the glass at 298.1°.

TABLE IV

ENTROPY DATA

	Selenium crystals	Selenium glass	Tellurium
Extrap. (0–50.1)°K.	2.26	2.61	3.54
Graph. (50.1–298.1)	8.23	8.54	9.31
$S_{0-298.1}$ graphical	10.49 ± 0.4	11.15 ± 0.4	12.85 ± 0.5
$S_{0-298.1}$ calcd. from functions	10.4	10.8	12.8

Summary

The heat capacities of selenium crystals and tellurium from about 50 to 300°K. have been determined and their corresponding entropies calculated as 10.49, and 12.85, respectively. Measurements for selenium glass over the same range indicate the difference in entropy from 0 to 298.1° for this material to be 11.15.

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[5] Eastman and McGavock, THIS JOURNAL, 59, 145 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Photolysis of Azomethane

BY MILTON BURTON, THOMAS W. DAVIS AND H. AUSTIN TAYLOR

In an investigation begun in this Laboratory it was hoped to use free methyl radicals formed in the photolysis of azomethane to induce chains in acetaldehyde at temperatures below that at which thermal decomposition could proceed. Inasmuch as previous investigators appeared to be quite certain of the mechanism of the decomposition of azomethane, it appeared likely that absolutely accurate information might be obtained about the length of chains initiated by free radicals.

According to Ramsperger[1] both the pyrolysis and the photolysis of azomethane proceed according to the over-all reaction

$$CH_3N{=}NCH_3 \longrightarrow C_2H_6 + N_2$$

with the latter having a quantum yield of about 2.0. Forbes, Heidt and Sickman[2] have challenged the latter figure and have produced evidence which, they claim, indicates that the quantum yield approaches 1.0 as an upper limit at pressures around 100 mm.; at higher pressures the quantum yield is reduced to a much lower figure by deactivating collisions. Heidt and Forbes[3] later published a statement on the products of pyrolysis and photolysis which indicated that methane was formed to a large extent in the later course of the decomposition. This conclusion was based upon pressure measurements at room temperature, -78.5, and $-183°$.

Leermakers[4] on the basis of experiments involving the simultaneous pyrolysis of lead tetraethyl and azomethane, concluded that neither decomposition affected the other and that consequently the ethyl radicals known to be produced in the decomposition of the former[5] were not initiating chains in the latter. It was suggested that, inasmuch as methyl radicals might be expected to behave similarly to ethyl radicals, methyl radicals likewise would not initiate chains at 270° and less. The work of Leermakers[6] and that of F. O. Rice and Evering[7] employing the mirror methods of Paneth[8] had shown that in all probability the reaction proceeded by a primary mechanism

$$CH_3N{=}NCH_3 \longrightarrow N_2 + 2CH_3$$

Consequently, Leermakers concluded that the decomposition of azomethane is not a chain reaction. O. K. Rice and Sickman[9] reached the same conclusion from their own work and that of Forbes, Heidt and Sickman.[2]

These conclusions of previous investigators seemed so decisive that it appeared only necessary to measure the nitrogen yield in the photolysis of azomethane in order to determine accurately the number of methyl radicals produced; the nitrogen determination was conducted because of the conclusions of Heidt and Forbes[3] that reaction 1 does not represent the over-all reaction.

The analyses conducted in this work changed the course of the investigation completely. It was found impossible to reconcile the amount of nitrogen formed with the proportions of the hydrocarbon products. The results of actual analyses given below indicate that many of the conclusions reached by previous investigators solely on the basis of pressure changes may require some modification. Pending the establishment of other data it does not seem feasible to use the photolysis of azomethane as a source of known quantities of methyl radicals.

Experimental Method

Azomethane.—The azomethane was prepared by the method of Ramsperger[1] except that the symmetrical dimethylhydrazine dihydrochloride was prepared according to the method of Hatt.[10] In our more recent preparations the mercury cut-offs recommended by Ramsperger were eliminated and large stopcocks were used. It was found that the yield of azomethane could be improved by reducing the pressure of the system initially to such a point that the azomethane would distil out of the preparation flask as soon as formed. As with previous investigators it was found that the principal impurities were probably moisture and air (perhaps nitrogen). Care must be taken that the former is not drawn from the drying tubes into the azomethane by the liquid air used for condensation. The entrapment of nitrogen in the condensed azomethane was best avoided by distilling toward the evacuating system from a dry-ice–toluene mixture to liquid air. In distilling

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[1] Ramsperger, THIS JOURNAL, **49**, 912, 1495 (1927).

[2] Forbes, Heidt and Sickman, *ibid.*, **57**, 1935 (1935).

[3] Heidt and Forbes, *ibid.*, **57**, 2331 (1935).

[4] Leermakers, *ibid.*, **55**, 4508 (1933).

[5] Paneth, *Ber.*, **62**, 1335 (1929); **64**, 2702, 2708 (1931).

[6] Leermakers, THIS JOURNAL, **55**, 3499 (1933).

[7] F. O. Rice and Evering, *ibid.*, **55**, 3898 (1933).

[8] *Cf.* F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins University Press, Baltimore, Md., 1935.

[9] O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

[10] Hatt, "Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., **16**, 18 (1936).

backward through a stopcock to dry-ice–toluene the liquid air was removed and the system was opened to a large reservoir. This enabled most of the nitrogen to escape into the reservoir. The stopcock to the dry-ice–toluene receiver was then closed and the reservoir was opened to the pumping system. After this the azomethane was again distilled forward from the dry-ice–toluene to the liquid air. This operation was repeated about six times (after about fifteen other distillations). At the end it was concluded that various samples distilled from the approximately 6 cc. of azomethane so formed (using four times the quantities indicated by Ramsperger) were reasonably pure.

It was not practicable to obtain true vapor pressure data. With the small amounts of our samples it was found that traces of grease or other impurity present in the reservoirs, might cause one fraction to present two different vapor pressures in two different reservoirs. Different fractions of the same 6-cc. yield all had vapor pressures between 744 and 756 mm. at 0° in different reservoirs. All together the various readings indicated that the last fraction was substantially like the first.

Light Source.—The light source used throughout these experiments was a constricted mercury arc of the type described recently.[11] Unless otherwise noted there was interposed between the light source and the reaction system a Corning No. 534 blue nultra filter. According to the specifications this filter transmits only wave lengths longer than 3500 Å. In all the experiments except the one at −22.5° the arc was located 2.5 cm. from the reaction vessel; at −22.5° the arc was 3.3 cm. from the reaction vessel.

Reaction Vessel and Thermostat.—The reaction vessel was a Pyrex flask of 1015-cc. volume connected to the vacuum system, the manometer, and the gas analysis system by means of capillary tubing closed off with simple greased stopcocks. The thermostat was a Pyrex beaker to which the filter was affixed in most of the experiments. The temperature was maintained manually at 20° or (in one experiment) at −22.5°. The total thickness of Pyrex between the arc and the reacting gas was of the order of 2 mm. This thickness transmits only at more than 2900 Å., transmitting the 3130 mercury line and the 3020 and 2960 to a slight extent.

Gas Analysis.—A Fischer Scientific Co. Gas Analysis Apparatus was permanently connected to the reaction system, through a mercury gas buret, a Töpler pump, and a trap. The large volumes of azomethane used made possible analyses on a macro-scale. The products of the decomposition were separated into condensable and non-condensable portions in the liquid air trap, measured in the mercury buret, bubbled through an auto-bubbler pipet (of the type described by Burton and Davis[12]) containing hydrochloric acid, and measured again over water. The hydrochloric acid was removed for analysis after each experiment. Any azomethane residue was removed by acid stannous chloride solution in an auto-bubbler pipet. Other pipets contained potassium hydroxide (for removing carbon dioxide and other acid gases), chromous chloride, and potassium pyrogallate (for the direct determination of residual oxygen after the combustions). Hydrogen was determined by cupric oxide oxidation while the volume of paraffin gases and the average value of n in the formula C_nH_{2n+2} were determined by oxidation over a hot platinum wire with subsequent measurements of the volume before and after bubbling through potassium hydroxide. After the removal of the unused oxygen, the fraction of nitrogen in the sample was calculated from the volume of the residual gas. Corrections were made, of course, for the nitrogen initially present in the oxygen.

The procedure of dividing the gases into condensable and non-condensable portions made it possible to determine approximately the amounts of methane, ethane and propane in the original gas. Naturally, the amounts of ethane and propane may be in error. They involve the assumption that these gases are the only saturated hydrocarbons in the condensed gas sample, while the calculated n might actually be the average for a mixture of ethane and some much higher hydrocarbon. Furthermore, it will be shown below that even in the non-condensable gases there is the possibility that the presence of some other hydrocarbon may require a recalculation of the results.

Photolysis of Azomethane.—Ordinarily, the azomethane was stored in a small reservoir immersed in a dry-ice–toluene mixture. The reservoir and its contents were constantly shielded from the light except when the cooling mixture was deliberately removed to permit distillation of the sample. In fact, during the whole course of the investigation the room was darkened to avoid the entrance of daylight. Preceding each run a sample was distilled into the reaction vessel, which was maintained at a constant temperature of 20°, and the initial pressure was determined. The reaction vessel was exposed to the arc when the latter had become steady at 4 amperes with the arc stretched through the capillary as previously described.[11] At the conclusion of each run the gas was permitted to stand in the vessel for at least five minutes to obtain check readings. In a few cases the gas stood for as long as three days without affecting the pressure.

Successive samples were withdrawn through the liquid air trap where they were fractionated into condensable and non-condensable portions and analyzed as already described. The results of these analyses for different fractions decomposed and different initial pressures are summarized in Table I.

In both Tables I and II P_0 is the initial pressure of the gas in the reaction vessel in mm. and P_F the final pressure. ΔP is the pressure change during the photolysis. All ratios, for example, $\Delta P/P_0$, are expressed in per cent. V_A is the volume of gas in cc. measured over water after all azomethane or possible alkaline gas has been removed by successive treatments with hydrochloric acid, stannous chloride and potassium hydroxide (the latter to remove acid vapors). V_G is the calculated volume of di-acid (alkaline) gas in the sample based upon titration of the hydrochloric acid in the first auto-bubbler pipet. The values are extremely variable; the reason for the variation will be explained below. V is the volume of gas after the photolysis measured over mercury before any chemical treatment. Mention should be made of the fact that, except for V, volumes (in Table II) are given only for moist gases. The values for N_2/V as given in Table I are corrected for moisture in the nitrogen so that the percentage given is the true one. The other percentages involving

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[11] Burton, THIS JOURNAL, **58**, 1645 (1936).

[12] Burton and Davis, *Ind. Eng. Chem., Anal. Ed.*, **9**, 139 (1937).

TABLE I

SUMMARY OF ANALYTICAL RESULTS

Experiment	22	16[c]	19	26	27	29	20	24	30[d]	31[e]	25	28
P_0	101.6	99.8	100.6	100.3	100.7	99.0	57.8	51.0	49.7	48.4	25.0	13.5
$\Delta P/P_0$	4.9	10.1	9.4	9.8	20.1	85.8	17.5	19.2	19.6	20.4	38.0	58.7
Unsat./V_A	0	0	0.7	0	0.5	0.4	0.7	0.8	0.8	0.4	0.8	0.9
CH_4/V_A	0	1.2	3.2	4.8	8.0	4.4	0.6	1.4	1.1	...	3.7	...
C_2H_6/V_A	41.0	44.8	40.9	40.0	39.0	36.8	45.3	42.1	44.7	...	42.2	...
C_3H_8/V_A[a]	1.5	0	0	0	0	7.9	0	0	0	...	0.3	...
N_2/V_A	58.2	55.5	54.8	56.3	53.8	52.0	53.9	56.6	53.1	55.4	53.2	53.3
Total	100.7	101.5	99.4	100.1	100.3	101.7	100.5	100.8	99.7	...	100.2	...
M or D[b]	M	M	M	M	M	D	D	D	D	M	M	M
V_G	33.9	...	...	2.9	2.7	0.45	3.7	14.5	1.1	0.85	1.7	0
$N_2/V = a$	5.4	11.5	10.1	10.2	18.1	47.8	16.1	18.0	17.3	18.3	28.6	38.1
$\Delta P/P_F = b$	4.7	9.2	8.5	8.9	16.7	46.2	14.9	16.1	16.3	17.0	27.3	36.9
a/b	1.15	1.25	1.19	1.15	1.08	1.03	1.08	1.12	1.06	1.08	1.05	1.03

N_2/V_A average = 54.7.

[a] This is an idealized figure presumed from the value of n in those cases where n has been determined on the residue condensed in liquid air. [b] N_2 by actual measurement = M; by difference = D. [c] In expt. 16 no effort was made to separate the product into condensable and non-condensable fractions by means of liquid air. [d] Expt. 30 was conducted with unfiltered light. [e] Expt. 31 was conducted at *ca.* −22.5° with unfiltered light.

TABLE II

DETAILED SUMMARY OF TWO ANALYSES

Experiment	28			31		
	F_N[a]	F_C[a]	Total	F_N	F_C	Total
P_0	..	...	13.5	..	...	48.4
$\Delta P/P_0$	..	...	58.7	..	...	20.4
V	11.4	17.5	28.9	15.2	66.2	81.4
V_A	11.0	10.2	21.2	14.5	13.1	27.6
Contraction	0.8	23.2		1.1	30.9	
Absorption	1.2	17.8		1.5	26.7	
n	?	1.865		?	2.28	
O_2 used, cc.	1.6	31.3		1.9	45.6	
N_2, cc.	10.3	1.0	11.3	14.1	1.2	15.3
CH_4, cc.		1.38			...	
C_2H_6, cc.		8.24			8.43	
C_3H_8, cc.		...			3.28	
Unsat./V_A			0.9			0.4
CH_4/V_A		6.5			...	
C_2H_6/V_A		38.8			30.5	
C_3H_8/V_A		...			11.9	
N_2/V_A			53.3			55.4
V_G			0			0.85

[a] F_N represents the fraction not condensed by liquid air; F_C represents the condensed fraction.

V_A are, of course, self-corrected. Although hydrogen was looked for in every experiment none ever was found.

It will be noticed that for experiments 28 and 31 data on the alkane content have been omitted. The detailed summary for those two is shown in Table II.

The volume of oxygen used is that required for the oxidation of the hydrocarbon gases. The *contraction* is the decrease in volume in cc. due to water formation during the combustion and the *absorption* represents the volume of carbon dioxide formed at the same time. n is the calculated value in the hypothetical mixed alkane C_nH_{2n+2}. The figures given for the alkanes are evidently idealized; they are based on the assumption that only two gases are present in the sample analyzed: in the uncondensed fraction—methane and ethane, and in the condensed—ethane and propane. In both experiments 28 and 31 the values for the contraction and absorption in the uncondensed fraction are so unusual as to preclude the calculation of a significant value for n. The results are presented for what they are worth without an attempt at interpretation other than the remark that a compound such as acetylene might account for the effect; however, acetylene would not be expected to pass the bromine pipet. It is possible that the high value for n in the condensable fraction of expt. 31 may be due to the presence of such a gas and that the computed value for propane is consequently wrong. In any event, the percentage given for propane or the presence of an equivalently large quantity of such another gas would be enough to differentiate expt. 31 (which was conducted at −22.5°) from all the other experiments. Judging from the small volumes of the contraction and the absorption in both experiments it is apparent that even if the actual hydrocarbons in the uncondensed portion were known the percentages reported would be only slightly changed.

As Ramsperger, and Forbes, Heidt and Sickman, have noted, it was found that when the photolysis was conducted at shorter wave lengths, as in experiments 30 and 31, a solid deposit settled on the walls of the reaction vessel; the deposit in experiment 31 (at −22.5°) was much lighter than in experiment 30. When the reaction vessel was removed for cleaning, the deposit disappeared completely, probably due to oxidation by the inrushing air.

Photolysis of Azomethane plus Acetaldehyde.—In some early experiments, in which azomethane was photolyzed in the presence of acetaldehyde using the blue nultra filter, it was found that, in a time which later experience demonstrated was sufficient to cause about 20% pressure increase ($\Delta P/P_0$) in pure azomethane, no acetaldehyde was decomposed at 20° according to the analyses. This result was in line with the conclusions of Leermakers on chain lengths in the photolysis of acetaldehyde at low temperatures[13] and was, of course, expected. The formation of a fog in the reaction vessel during runs and the deposition of an extremely viscous, non-volatile material was, however, unexpected. In the case mentioned the results are summarized in Table III. The method of calculation is obvious from the table. The following were known by measurement at the end of the photolysis: the initial pressures of the acetaldehyde and the azomethane, the volume of the reaction vessel (1015 cc.), the weight of acetaldehyde in the deposit (determined by Ripper's method[14]) and the total pressure change. The value for N_2/V was determined by difference after analysis of the resultant gases. However, as is shown in Table III, there are sufficient data for a calculation of N_2/V on the assumption that the average value for a/b calculated in Table I for $\Delta P/P_0 = 20\%$ holds in this case also. The check between the observed and the calculated values for N_2/V is good. No allowance has been made in these calculations for a pressure decrease due to a loss of azomethane from the vapor phase by inclusion chemically or otherwise, in the deposit. This was not deemed necessary since the agreement between the observed and calculated nitrogen values would indicate that the deposit contained solely acetaldehyde. The conclusion may be drawn from Table III that, for every 3.3 molecules of nitrogen liberated, approximately two molecules of acetaldehyde are lost by an association reaction.

TABLE III

SUMMARY OF EXPT. 5. AZOMETHANE PLUS ACETALDEHYDE AT 20°

Initial pressure CH_3CHO, obsd., mm.	104.2
Initial weight CH_3CHO, calcd. = c, g.	0.255
Wt. CH_3CHO in deposit (by analysis) = d, g.	.042
d/c, %	16.5
ΔP_A (due to CH_3CHO) calcd., mm.	−17.2
$\Delta P_{\text{obsd.}}$[a], mm.	7.2
ΔP (due to CH_3NNCH_3) calcd., mm.	24.4
P_0 = initial pressure CH_3NNCH_3, obsd., mm.	106.3
$\Delta P/P_0$, %	22.9
$\Delta P/P_F$ (= b) from $\Delta P/P_0$, %	18.6
a/b from Table I (assumption)	1.08
N_2/V (= a) calcd., %	20.1
N_2/V by analysis (approximate), %	19.9
V (at 760 mm., 20°) calcd., cc.	173.8
N_2, calcd., cc.	35.0
CH_3CHO (at 760 mm., 20°) in deposit, cc.	21.2

[a] $\Delta P_{\text{obsd.}}$ is the final total pressure increase on prolonged standing after the completion of the run. The figure given is somewhat lower than that immediately at the completion of the run before the fog had a chance to settle. The value at that time was 11.6 mm.

It was noticed that the deposit had a faint musty odor similar to that of aldehyde ammonia and was quite readily soluble in water without change of odor. When a small amount of hydrochloric acid was added, the odor of acetaldehyde was quite strong.

The formation of the deposit is definitely linked to the photolysis of azomethane for blank runs with acetaldehyde alone were without effect and prolonged standing of mixtures of the two gases without illumination was also without results.

Rate of Photolysis of Azomethane.—With the exception of experiments 30 and 31 in which unfiltered light was used, the conditions of light intensity during the photolyses were fairly well reproduced in most experiments. The arc was maintained constant at 4.0 amperes and was cooled constantly with running water. The distance from the arc to the reaction vessel was rigidly fixed. While no photometer readings were taken there is no reason to expect a large order of variation between experiments on the basis of light intensity alone. Consequently, the pressure–time relationships during the photolyses of azomethane are of some significance if the different experiments are considered relatively to each other.

Neglecting for the moment the effect of decreased light absorption by azomethane as the reaction proceeds, it is evident that the rate of change of partial pressure of azomethane may be represented by the equation

$$\mathrm{d}p/\mathrm{d}t = Kp$$

or

$$\ln P_0/p_t = Kt$$

where P_0 is the initial pressure of the system, p is the partial pressure of azomethane (when $t = 0$, $p = P_0$) and p_t is the partial pressure of azomethane at time t. Now, if $p_{N_2,t}$ be the partial pressure of nitrogen at time t

$$p_{N_2,t}/p_t = V_{N_2,t}/V_t$$

where P_t is the observed pressure and V_t the total measured volume at time t, while $V_{N_2,t}$ represents the volume of nitrogen as determined by actual analysis. But, from Table I, ($V_{N_2,t}/V_t$ and N_2/V are the same)

$$p_{N_2,t}/P_t = \frac{a}{b} \times \frac{\Delta P}{P_t}$$

and

$$P_{N_2,t} = \frac{a}{b} \times \Delta P$$

But

$$p_t = P_0 - P_{N_2} = P_0 - \frac{a}{b}\,\Delta P$$

Consequently

$$\ln \frac{P_0}{P_0 - a/b\ \Delta P} = Kt$$

In Fig. 1, a curve is plotted showing the relation between a/b and $\Delta P/P_0$ (see Table I) where the

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(13) Leermakers, THIS JOURNAL, **56**, 1537 (1934).

(14) *Cf.* Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1929, pp. 450–452.

latter is indicated in per cent. The values of a/b, as taken from this curve, were used in plotting the rate curves in the three experiments illustrated in Fig. 2. It is seen that the initial portion of each curve follows a straight line, as may be expected, but that the rate later falls off. In experiment 28, where $P_0 = 13.5$ mm., this departure from linearity is evident sooner than in experiment 29, where $P_0 = 99.0$ mm. The values for K during the linear (initial) portions of the curves, as determined from Fig. 2 and similar plots, are summarized in Table IV.

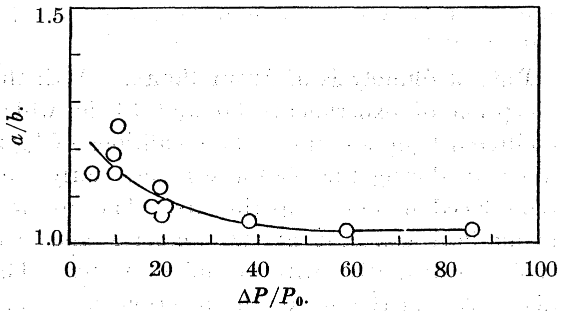

Fig. 1.—Relationship between a/b and $\Delta P/P_0$, the latter being expressed in per cent.

TABLE IV

Experiment	P_0	$K \times 10^3$
21	100.7	1.66
22	101.6	1.69
23	101.0	1.63
26	100.3	1.40
27	100.7	1.57
29	99.0	1.38
20	57.8	1.65
24	51.0	1.67
25	25.0	1.85
28	13.5	1.88

There appears to be a slight drift toward higher K values at lower initial pressures. This is in the direction which might be expected on the basis of relative probabilities of light absorption and confirms the measurements of Goldfinger.[15]

Discussion of Results

The analyses reported here are the first complete ones recorded in the literature of azomethane since those of Thiele,[16] who examined the products both of explosion and of complete decomposition in a hot tube.

The most significant feature to be observed at the outset is that the percentage of nitrogen in the yield of gases insoluble in acid, averages 54.7% regardless of the stage of reaction at which the analysis is made. This excess of nitrogen over that expected from a simple decomposition of azomethane suggests that azomethane may be removed from the system by some means other than decomposition to yield nitrogen. Hence the use of the amount of nitrogen as a measure of the azomethane disappearing may be invalid. Such an assumption was actually made in calculating the data in Table IV. Furthermore, the use of pressure change observed during reaction, as a measure of the azomethane decomposed, also requires further consideration.

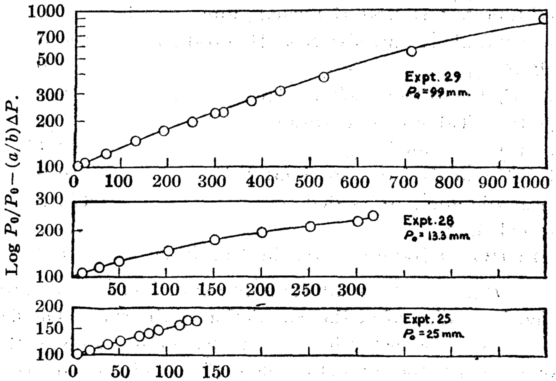

Fig. 2.—Rate of photolysis according to equation 1.

The simplest assumptions of the primary step in the decomposition appear to be either

$$CH_3N{=}NCH_3 + h\nu \longrightarrow C_2H_6 + N_2 \quad (1)$$

or

$$CH_3N{=}NCH_3 + h\nu \longrightarrow 2CH_3 + N_2 \quad (2)$$

the one yielding stable molecules of nitrogen and ethane by a rearrangement of the suitably activated azomethane; the other yielding free radicals by disruption of C–N bonds. Such a reaction as

$$CH_3N{=}NCH_3 + h\nu \longrightarrow CH_3 + N{=}NCH_3 \quad (3)$$

has little probability,[17] although not denied, it will not be further considered here, as the ultimate fate of the radical $NNCH_3$ would be pure conjecture. Furthermore, in the hydrolysis of azomethane Thiele[16] finds the principal products to be formaldehyde and methylhydrazine, which result would suggest a possible isomeric form of azomethane of the type $CH_2{=}N{-}NH{-}CH_3$. The decomposition of such an isomeric form might be expected to give readily a radical with an ability to confer definite basic properties

$$CH_2{=}N{-}NH{-}CH_3 + h\nu \longrightarrow CH_2N{-}NH + CH_3 \quad (4)$$

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(15) Goldfinger, *Compt. rend.*, **202**, 1502 (1936).

(16) Thiele, *Ber.*, **42**, 2575 (1909).

(17) *Cf.* Patat, *Naturwissenschaften*, **23**, 801 (1935).

TABLE V

COMPARISON OF ALKANE YIELD AND PRESSURE INCREASE

Expt.	P_0	V	V_{Alk}	V_0 (calcd.)	$V-V_{Alk}$	V_{Alk}/V_0, %	$V_{Alk}/(V-V_{Alk})$, %	$\Delta P/P_0$, %
22	101.6	141.4	5.6	135.9	135.8	4.1	4.1	4.9
16	99.8	143.3	13.6	133.2	129.7	10.2	10.0	10.1
19	100.6	148.0	12.0	134.5	136.0	8.9	8.8	9.4
26	100.3	144.6	11.8	134.1	132.8	8.8	8.9	9.8
27	100.7	160.1	25.3	134.5	134.3	18.8	18.8	20.1
29	99.0	252.8	113.5	132.2	139.3	86.0	81.5	85.8
20	57.8	89.9	12.4	77.3	77.5	16.0	16.0	17.8
24	51.0	79.7	11.0	68.2	68.7	16.1	16.0	19.2
30	49.7	78.7	11.8	66.5	66.9	17.7	17.6	19.6
25	25.0	45.6	11.2	33.4	34.4	33.5	32.6	38.0

The fate of the methyl radicals produced in any of the above reactions is likewise as doubtful as the primary step for azomethane. The simplest course would be the production of ethane. The possibility nevertheless exists of such a chain reaction as

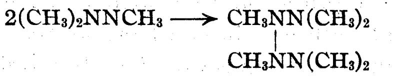
$$CH_3 + CH_3N{=}NCH_3 \longrightarrow C_2H_6 + N_2 + CH_3 \quad (5)$$

even though the work of previous investigators indicates its improbability. On the other hand, an addition of CH_3 to azomethane seems never to have been considered

$$CH_3 + CH_3N{=}NCH_3 \longrightarrow (CH_3)_2NNCH_3 \quad (6)$$

$$CH_3 + (CH_3)_2NNCH_3 \longrightarrow (CH_3)_2NN(CH_3)_2 \quad (7)$$

or



$$2(CH_3)_2NNCH_3 \longrightarrow \begin{array}{c} CH_3NN(CH_3)_2 \\ | \\ CH_3NN(CH_3)_2 \end{array} \quad (8)$$

The only definite statement that can be made is that the reaction may be much more complicated than has been assumed previously.

Of the above reactions, 8 is the only one which would involve a pressure decrease and does not appear highly probable. In the other reactions, the pressure either increases or is unchanged. It may be concluded therefore that the pressure increase occurring during the decomposition is due to the formation of alkane molecules. The data in Table V substantiate this.

P_0, V and ΔP have the significance previously indicated. V_{Alk} is the total volume of dry alkane gases as determined by analysis. V_0 is the initial volume of azomethane calculated to 760 mm. and 20° approximately the conditions at the time of the gas analysis. The correspondence between V_0, a calculated value, and $V-V_{Alk}$, a measured one, indicates that the pressure increase is to be accounted for by the alkane produced. It is, however, apparent that in some cases there is a discrepancy between the ratios in the last three columns, especially in the values of $\Delta P/P_0$. The only satisfactory explanation of this appears to lie in the doubtful accuracy of ΔP which, involving as it does a difference, frequently small relative to P_0, is correspondingly less accurate. This error, however, does not affect the validity of any of the calculations reported above.

Comparing now those cases of small decomposition, where $\Delta P/P_0$ is no greater than 20%, the nitrogen formed averages 55.3% while the alkane formed, calculated as ethane, averages 44.4%. Evidently some compound is produced during the reaction which has a higher carbon to nitrogen ratio than that in azomethane. Reaction 7 above presents such a possibility. Assuming that such a possibility requires free methyl radicals it would appear that out of five molecules of azomethane *decomposing* to give nitrogen, only four give alkane and hence *at least* one of them must have yielded methyl radicals.

Turning to the results in Table III on the photolysis of azomethane in presence of acetaldehyde, it is seen that for every two molecules of acetaldehyde precipitated (presumably as a polymer) 3.3 molecules of nitrogen were produced from the azomethane. If every methyl radical is assumed involved in the polymerization of two aldehyde molecules, it would appear that of every 6.6 molecules of azomethane decomposed, one decomposed yielding free methyl radicals.

It should be realized that the latter figure of one in 6.6 would tend to be a maximum ratio, while the former 1 in 5 is a minimum. The agreement is by no means perfect but is sufficiently significant to suggest that azomethane may not decompose entirely into nitrogen and free methyl radicals.

With regard to the possible existence of some compound formed with azomethane and methyl radicals, reference to Table I will show values of V_G, the volume of gas, assumed di-acid, calculated from the titration of the hydrochloric acid used in the first absorption pipet. As already stated the values are extremely variable since it was not at first realized that the hydrolysis of azomethane was rapid enough to cause interference. The values for the later experiments were obtained as rapidly as possible after the exit gases from the decompositions had been washed with the acid, the time of contact between the undecomposed azomethane and acid being as short as practicable. The results definitely indicate some basic material present. In experiments 28 and 29, corresponding to over 50 and 80% decomposition, the amount of this basic material is very small and the values of V_G may be due simply to azomethane hydrolysis. It should be noted further that in precisely these experiments the discrepancy between nitrogen and alkane produced is by no means as large as that discussed above for decompositions amounting to less than 20%. In experiment 29 the nitrogen value is 52% while the alkane calculated as ethane is approximately 51%. In addition to this evidence, is the formation of the deposit during photolysis at shorter wave lengths. The observation already mentioned that the deposit disappeared immediately on contact with air is in line with the known easy oxidation of many hydrazines.[18]

The belief that methyl radicals are without effect on azomethane rests largely on Leermakers' study of the simultaneous thermal decomposition of azomethane and lead tetraethyl.[4] Leermakers calls attention to the falling off in the rate constant for the decomposition of lead tetraethyl of some 25% at 260° in presence of azomethane. This is calculated from the over-all pressure change observed assuming the azomethane pressure change to be found in pure azomethane. No interpretation is offered of the falling off since Leermakers' primary object was to discover the presence of chains initiated by the ethyl radicals from the lead tetraethyl in the azomethane. Such chains would have caused a rising constant. An examination of his data at 275° shows a similar 10 to 15% falling off. The decrease in rate constant finds a ready explanation on the basis of one conclusion from this study, namely, that ethyl radicals could disappear by addition to azomethane whereas Leermakers assumes the ultimate fate of all the ethyls to be butane. Two possibilities, however, present themselves: either, all the lead tetraethyl decomposes into free radicals and only a part of them combine with azomethane, or, part of the lead tetraethyl decomposes to form butane directly. If the latter were true, it would be expected that the proportion of lead tetraethyl decomposing into radicals would be greater the higher the temperature and that therefore the greater would be the effect of azomethane. Actually, however, the effect of azomethane is less at 275 than at 260°. Hence it must be concluded that not all of the ethyl radicals react with azomethane at these temperatures. Such a result is not necessarily true at lower temperatures though it would appear reasonable to conclude that there also some of the methyl radicals may actually combine to give ethane and hence that our results do not prove decisively that azomethane does decompose to give nitrogen and ethane directly. Allen and Sickman[19] in studying the azomethane induced decomposition of acetaldehyde came to the conclusion that the chain length varied between 500 at 244.8° and 22 at 328.7°. If the conclusion be derived from our work that azomethane does not decompose exclusively by a free radical mechanism it appears that the calculated figures for the chain length may be considerably too low, since fewer but longer chains would not be required to explain the effects observed. This would be in line with Leermakers' estimate[13] of quantum yields of about 300 in acetaldehyde at 309.5°. In the latter case also, the chain length based upon free radical production would be higher than the figure given because it would be expected that during photolysis most of the acetaldehyde decomposes by a rearrangement mechanism.[20] It now appears that in many of those reactions where clear-cut rupture into free radicals or alternatively clear-cut rearrangement to form stable molecules was thought to be occurring, actually both processes might have been taking place. Formic acid dissociates into stable molecules[21] but acetic acid apparently gives both stable molecules[22] and free radicals.[11] Formaldehyde gives stable molecules[23]; acetaldehyde apparently dissociates in

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[18] Taylor and Ditman, *J. Chem. Phys.*, **4**, 214 (1936).

[19] Allen and Sickman, THIS JOURNAL, **56**, 2031 (1934).

[20] Blacet and Roof, *ibid.*, **58**, 278 (1936); Rollefson, *J. Phys. Chem.*, **41**, 259 (1937); Burton, *ibid.*, **41**, 322 (1937).

[21] Gorin and H. S. Taylor, THIS JOURNAL, **56**, 2042 (1934); Burton, *ibid.*, **58**, 1655 (1936).

[22] Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 124 (1932).

[23] Locker and Patat, *ibid.*, **B27**, 431 (1934).

both ways.[20] The results of this work indicate that azomethane may resemble acetaldehyde and acetic acid in its tendency to suffer both rupture and rearrangement.

Forbes, Heidt and Sickman[2] showed that the quantum yield of decomposition of azomethane (based upon pressure measurements) approached a value of unity at low pressures (*i. e.*, in the neighborhood of 100 mm.) and apparently decreased both at longer wave lengths (about 3660 Å.) and with increasing pressure. Their measurements appear to have been made on only three or four different samples of azomethane; several runs at different wave lengths and successively decreasing partial pressures of azomethane were made with the same sample. Our results would indicate that the partial pressures of azomethane as calculated by them were too high and that a correction should be made for azomethane disappearing in an association reaction with methyl. This would tend to bring up the quantum yields. Whether it would bring the quantum yields up to unity we do not know; however, there is not very much concordance between their various results. The quantum yields as reported by them do decrease with successive runs on the same sample and our results indicate the reason why. Also, our work indicates a deposit of some product even at >3500 Å.; perhaps it is the formation of such a product which might account for the extremely low quantum yields they report in certain runs.

In conclusion, some mention should be made of our results both at low temperatures and in protracted runs. In both cases (experiment 31 at −22.5° and experiments 28 and 29 for long runs) it may be seen in Tables I and II that the propane yields (as idealized from the n values) are high. The explanation in the long runs is that the methyl radicals combine with some of the products to form the higher carbon compounds. In no case is there a simple replacement reaction such as

$$CH_3 + C_2H_6 \longrightarrow C_3H_8 + H \qquad (10)$$

for no hydrogen has been found in the analyses. To be sure, the reaction

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \qquad (11)$$

followed by

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \qquad (12)$$

or

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (13)$$

would account for the result. However, such considerations lie entirely in the realm of conjecture. Suffice it to say that the probability of that general type of reaction increases as the relative concentration of azomethane decreases.

Similarly, as the temperature is lowered, the probability of methyl radical adding on to azomethane by such a reaction as 7 decreases. Reactions such as 12 and 13 would then be favored; the analysis of Table II is in agreement with such an hypothesis.

Conclusion.—Methods heretofore used depending exclusively on pressure measurement for the calculation of the amount of azomethane decomposed photolytically have been in error. There is a greater amount of azomethane decomposed than is represented by the pressure increase. The amount of nitrogen formed for small decompositions exceeds the hydrocarbons produced. The evidence appears to indicate that azomethane decomposes by a rearrangement mechanism as well as by rupture into free radicals, which latter has hitherto been thought to be the exclusive path.

Summary

1. The results of a number of analyses of the products of the photolysis of azomethane have been reported.

2. In general, the amount of nitrogen produced exceeds the amount of hydrocarbon gas. The amount of higher hydrocarbon produced (expressed as propane) increases with degree of decomposition and at reduced temperatures. No hydrogen and but a small smount of unsaturated hydrocarbons are produced.

3. The results of some preliminary work with azomethane photolyzed in the presence of acetaldehyde are also reported. This work is being continued.

4. The results obtained are consistent with an hypothesis that azomethane does not decompose exclusively by rupture but that it may also decompose by a rearrangement mechanism to form stable molecules.

5. The hypothesis that some of the free methyl radicals formed react with azomethane to form an addition compound is consistent both with the results reported here and with the results of previous investigators.

6. The rates of the photolyses are in approximate agreement with what might be expected from the hypotheses offered as to the mechanism of the reactions.

UNIVERSITY HEIGHTS
NEW YORK, N. Y.

RECEIVED MARCH 20, 1937

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Studies on the Vapor Pressure–Temperature Relations of the Binary System Zinc Nitrate–Water

BY WARREN W. EWING AND H. M. FISHER

Vapor pressure data on the binary system zinc nitrate–water are presented in this article, which is a continuation of a series of similar studies being carried on in this Laboratory. Reports on the calcium nitrate system and the magnesium nitrate system have been published. The cadmium nitrate system is now being investigated. These systems are particularly suitable for these types of studies since, in general, they are quite stable over ordinary temperature ranges, they form various hydrates, they are quite soluble and the solutions can be supercooled readily, especially in the concentrated ranges. Due to this supercooling, vapor pressures can be measured on very concentrated solutions; up to 82% on the zinc nitrate system.

According to solubility studies,[1–3] zinc nitrate crystallizes with varying amounts of water, namely, $Zn(NO_3)_2 \cdot 9H_2O$ (T. P. = −17.6°), $Zn(NO_3)_2 \cdot 6H_2O$ (m. p. = 36.1°), $Zn(NO_3)_2 \cdot 4H_2O$ (m. p. 44.7°), $Zn(NO_3)_2 \cdot 2H_2O$ (m. p. 55.4°), $Zn(NO_3)_2 \cdot H_2O$ (m. p. 73.9°). Probably the anhydride also exists.[4] In this investigation, vapor pressures of two-phase systems (unsaturated and supersaturated solutions plus vapor), and the three-phase systems hydrated salt-saturated solution–vapor (in the stable and the metastable regions) and mixtures of two hydrated salts–vapor have been measured over the temperature range 20 to 60°.

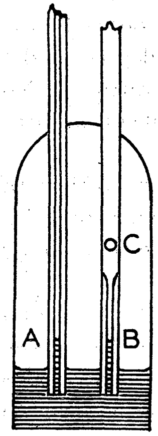

Fig. 1.—Tensimeter trap.

Preparation of Materials.—A c. p. grade of zinc nitrate was purified by three recrystallizations, first as tetrahydrate and subsequently twice as hexahydrate, from solutions containing a little nitric acid. The hexahydrate crystals were freed from excess water and nitric acid by continuous evacuation.

The unsaturated solutions for the vapor pressure experiments were made by dissolving the hexahydrate. The more concentrated solutions were made by evaporating the molten hexahydrate crystals at 80°. This resulted in some decomposition of zinc nitrate. Consequently, all solutions were adjusted to neutrality, where necessary, with 100% nitric acid, using brom thymol blue indicator.

Experimental

The vapor pressure measurements were made in a modified Smith–Menzies apparatus which was described in the magnesium nitrate article.[5]

The only alteration was the redesign of the dibutyl phthalate trap. The new design is illustrated in Fig. 1. A and B are two capillary tubes of identical bore. Consequently, when the pressures on the two sides of the dibutyl phthalate are the same, the liquid rises in A to the same height that it does in B due to capillary attraction. This makes the measuring of the difference from the true equilibrium height much easier. C is an opening through which air and vapor can pass. This arrangement also has an advantage in the measurement of pressures below one millimeter. In this low range the errors in measuring the difference in heights of two mercury columns are a large percentage of the total pressure. When the external system is evacuated completely, the dibutyl phthalate trap then serves as a manometer which is about thirteen times as sensitive as a mercury manometer, due to the different densities of the two liquids. This sensitivity is diminished somewhat due to the greater difficulty in measuring the exact position of the meniscus of dibutyl phthalate.

Vapor pressure studies were made on the following systems: (1) a mixture of hexahydrate and tetrahydrate crystals from below the eutectic temperature down to 10° (Table I); (2) a mixture of tetrahydrate and dihydrate crystals from the eutectic temperature down to 20° (Table II); (3) saturated solutions over the range from a saturated solution of hexahydrate at 10° to a saturated solution of dihydrate at 55° (Table III); (4) solutions ranging in concentration from 10 to 57% from 20 to 50°; solutions from 63 to 72% from 30 to 60°; and two solutions 80 and 82% from 35 to 60° (Table IV).

TABLE I

THE VAPOR PRESSURE OF A MIXTURE OF HEXAHYDRATE AND TETRAHYDRATE CRYSTALS

Temp., °C.	V. p., mm.
34	7.54
30	5.95
25	4.15
20	2.92
15	2.00
10	1.36

TABLE II

THE VAPOR PRESSURE OF A MIXTURE OF TETRAHYDRATE AND DIHYDRATE CRYSTALS

Temp., °C.	V. p., mm.
39	2.42
38	2.25
37	1.80
35	1.25
30	0.65
25	.27
20	.08

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(1) Ewing, McGovern and Mathews, THIS JOURNAL, **55**, 4827 (1933).

(2) Ewing, Ricards, Taylor and Winkler, *ibid.*, **55**, 4830 (1933).

(3) Sieverts and Petzold, *Z. anorg. allgem. Chem.*, **212**, 52 (1933).

(4) Marketos, *Compt. rend.*, **155**, 210 (1912).

(5) Ewing, Klinger and Brandner, THIS JOURNAL, **56**, 1053 (1934).

TABLE III

THE VAPOR PRESSURE OF SATURATED SOLUTIONS

Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.
Solid phase $Zn(NO_3)_2·6H_2O$		Solid phase $Zn(NO_3)_2·4H_2O$		Solid phase $Zn(NO_3)_2·2H_2O$	
10	4.25	34	7.54	37	1.80
20	7.27	35	7.95	38	2.00
25	9.01	36	8.36	39	2.15
30	10.76	38	8.74	40	2.24
33	11.45	40	9.18	42	2.36
34	11.55	42	9.14	45	2.48
35	11.42	43	9.02	50	2.44
36	10.55	44	8.56	55	2.06
36	9.66	44	5.73	$Zn(NO_3)_2·2H_2O$ Metastable	
35	8.15	43	4.21		
34	7.54	41	3.43	35	1.57
		39	2.42	30	1.15
		38	2.25	25	0.55
				20	.42

These data are shown in Fig. 2. Curve ABC represents the vapor pressure–temperature relations of saturated solutions of hexahydrate. Curve CEF represents saturated solutions of tetrahydrate, while FI represents saturated solutions of dihydrate. Curve FH represents saturated solutions of dihydrate in a metastable region. Curves CD and FG are, respectively, the mixtures of hexahydrate–tetrahydrate crystals, and tetrahydrate–dihydrate crystals. The remaining curves, numbers 1 to 15, represent vapor pressure–temperature relations of the solutions designated in Table IV. The points at which these curves cross ABC, CEF, and FI, are the freezing points of the various solutions. Supersaturation was obtained in a few cases, more easily for solutions supersaturated with respect to tetrahydrate than with the other hydrates.

TABLE IV

THE VAPOR PRESSURE OF SOLUTIONS OF ZINC NITRATE

Solution	Concn., %	M	Temp., °C.					
			20	30	40	50	60	
1	10.258	0.603	16.78	30.41	53.04	88.97		
2	18.466	1.196	15.99	29.24	51.00	85.62		
3	25.577	1.815	15.60	28.31	49.70	82.55		
4	26.434	1.897	15.12	27.31	48.34	80.24		
5	32.354	2.525	14.25	25.31	45.21	75.01		
6	34.618	2.796	13.62	25.17	44.07	72.60		
7	35.079	2.853	13.37	23.33	42.42	71.63		
8	44.045	4.156	11.05	19.98	35.19	59.49		
9	53.236	6.011	8.04	14.85	26.25	43.16		
10	57.362	7.103	6.30	11.45	20.32	35.55		
11	63.150	9.048		7.76	13.91	24.05	40.96	
12	67.514	10.973		4.75	8.74	15.17	26.21	
13	72.713	14.070		2.46	8.42	8.42	14.74	
			35	40	45	50	55	60
14	80.177	21.355	1.77	2.38	3.20	4.21	5.65	7.11
15	82.375	24.677	1.02	1.45	1.87	2.48	3.28	4.33

Solution 15 20° 0.37 25° 0.53 30° 0.75

The method of least squares was used on an equation of the form, $\ln p = A/T + BT + C$ to coördinate the data on the fifteen solutions in Table IV. The pressures were calculated at each temperature and usually showed less deviation than the probable errors computed for each set of readings at one temperature. After a consideration of all errors, it may be said that the data presented is accurate to 0.2%.

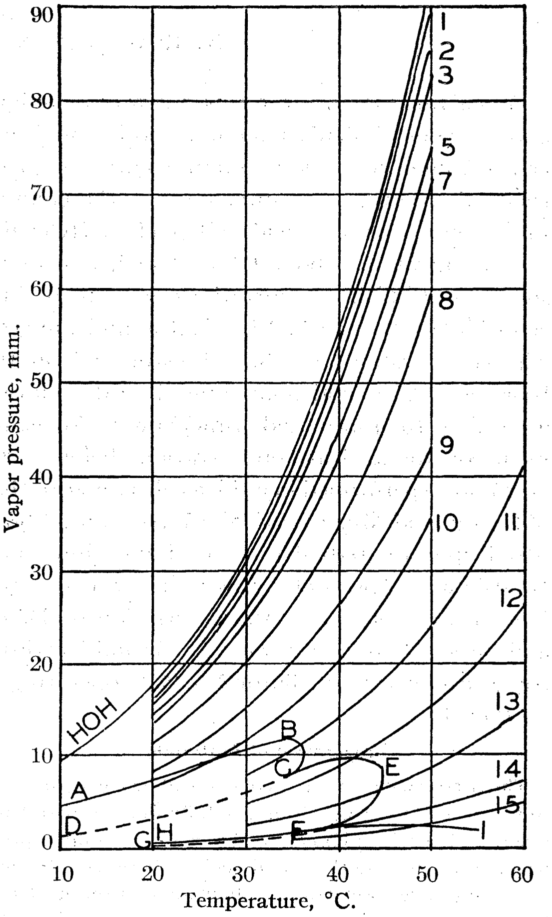

Fig. 2.

Vapor pressure measurements were not made at concentrations higher than 82%, which is the concentration of the saturated dihydrate solution at 50° (see Fig. 2), because at higher concentrations than this the zinc nitrate decomposed to such an extent that the data obtained were not reliable enough to warrant publication. This decomposition became noticeable at the higher temperatures above 82% concentrations. Consequently, the complete data for the dihydrate curve and the data on the monohydrate saturated solutions are not given.

Summary

Complete vapor pressure data on the system zinc nitrate–water from 0 to 82% concentration and from 10 to 60° are given. This includes vapor pressures for unsaturated, saturated and supersaturated solutions and for eutectic mixtures of crystals.

BETHLEHEM, PENNA. RECEIVED APRIL 6, 1937

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Ionization Constant of α-Crotonic Acid at 25° from Conductance Measurements[1]

BY BLAIR SAXTON[2] AND GEORGE W. WATERS

A general outline of the experimental technique and method of calculation employed in this study can be found in previous communications[3,4] from this Laboratory. Measurements of the conductance of α-crotonic acid ($CH_3CH{=}CHCOOH$) at concentrations above 0.002 demal, and of its sodium salt at all concentrations, were made in a cell of Type B described by Saxton and Langer.[3] The cell constant was 3.7261 estimated on the basis of a 0.1 demal potassium chloride solution according to Jones and Bradshaw.[5] Measurements on the acid at concentrations below 0.002 demal were performed in a silica cell similar to that of Saxton and Meier,[4] and of cell constant, 1.0830 based upon the 0.01 demal solution of Jones and Bradshaw.[5] The bridge was built by Leeds and Northrup according to the description of Dike,[6] and the source of power was a Leeds and Northrup Audio Frequency Oscillator No. 9842 operating at 1000 cycles.

Preparation of Materials

The α-crotonic acid was a commercial product subjected to five recrystallizations from carefully purified petroleum ether, and slowly sublimed. The white crystalline product was almost odorless, and melted between 71.5 and 71.7° according to measurements made in a simple Thiele tube with a recently calibrated thermometer. The value 71.4° was previously obtained in this Laboratory[7] from cooling curves with acid from the same source. The acid was stored in a vacuum desiccator over calcium chloride and suffered no appreciable change in melting point during the course of the conductance measurements.

The sodium salt was prepared from sodium carbonate (*ex* bicarbonate) and α-crotonic acid in sufficient excess to bring the resulting solutions to a *p*H of 6.7 to 7.0 on the basis of Lamotte standard buffers and brom thymol blue. Conductivities of these solutions were corrected[8] for the effect of the excess acid.

The experimental results, $\Lambda_{(\text{obsd.})}$, for sodium α-crotonate are recorded in Table I along with values derived from the semi-empirical equation[9]

$$\Lambda_{(C_4H_5O_2Na)} = 83.30 - 78.84\sqrt{c} + 97.27c(1 - 0.2276\sqrt{c}) \tag{1}$$

TABLE I

SODIUM α-CROTONATE

$c \times 10^3$	$\Lambda_{(\text{obsd.})}$	$\Lambda_{(\text{Eq. 1})}$
0.18773	82.13	82.24
.75176	81.19	81.21
1.6436	80.23	80.29
2.6083	79.45	79.52
2.8315	79.38	79.38
3.9861	78.68	78.71
4.5069	78.48	78.44
5.6194	77.95	77.93
7.2425	77.31	77.28
9.8864	76.46	76.40
14.735	75.19	75.12
20.222	74.04	73.99
23.334	73.49	73.45
29.457	72.48	72.52
32.616	72.08	72.10

The parameters of this equation were adjusted to fit the data by the method of least squares. Assuming the validity of the Kohlrausch principle, equation (1) may be combined with the expressions

$$\Lambda_{HCl} = 426.28 - 156.84\sqrt{c} + 169.7c(1 - 0.2276\sqrt{c}) \tag{2}$$

$$\Lambda_{NaCl} = 126.47 - 88.65\sqrt{c} + 94.8c(1 - 0.2276\sqrt{c}) \tag{3}$$

previously obtained in this Laboratory[10] to yield the relation

$$\Lambda_{C_4H_5O_2H} = 383.11 - 147.03\sqrt{c_i} + 172.2c_i(1 - 0.2276\sqrt{c_i}) \tag{4}$$

for the hypothetical completely dissociated α-crotonic acid at an ion concentration c_i.

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[1] This communication embodies part of the experimental material to be presented by George W. Waters to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] After Professor Saxton's death, June 16, 1936, this work was continued under the direction of Professor Benton B. Owen.

[3] Saxton and Langer, THIS JOURNAL, **55**, 3638 (1933).

[4] Saxton and Meier, *ibid.*, **56**, 1918 (1934).

[5] Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

[6] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[7] Saxton and Skau, THIS JOURNAL, **52**, 335 (1930).

[8] MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[9] Shedlovsky, *ibid.*, **54**, 1405 (1932).

[10] The values of the characteristic parameters determined by Saxton and Langer (ref. 3) have been altered slightly to conform to present cell constants; *cf.* ref. 5.

The experimental equivalent conductances, Λ_c, of α-crotonic acid solutions are recorded in Table II. The ion concentrations,[11] c_i, and the values of the dilution constants are also included. Multiplication of K'

$$K' = c_i^2/(c - c_i) \quad (5)$$

by the activity coefficient ratio, y_i^2/y_u, should yield the thermodynamic ionization constant, K, but because of the approximations introduced in the calculation of K', and our use of[11]

$$\log (y_i^2/y_u) = -1.013\sqrt{c_i} \quad (6)$$

for estimating the unknown activity coefficients, the values of K recorded in the last column of Table II are not independent of the concentration. Fortunately the variation in log K is linear in $c_u (= c - c_i)$, which readily permits evaluation of the true thermodynamic constant by the extrapolation[12] illustrated in Fig. 1.

TABLE II

α-CROTONIC ACID

$c \times 10^3$	Λ_c	$c_i \times 10^3$	$K' \times 10^5$	$K \times 10^5$
0.95825	51.632	0.12970	2.0303	1.9771
1.7050	39.473	.17655	2.0394	1.9771
1.8047	38.343	.18154	2.0304	1.9676
3.2327	29.083	.24686	2.0410	1.9675
4.0138	26.249	.27675	2.0495	1.9715
4.9736	23.677	.30942	2.0527	1.9702
4.9974	23.602	.30992	2.0491	1.9667
5.8329	21.926	.33614	2.0556	1.9695
7.1422	19.861	.37297	2.0550	1.9645
10.259	16.652	.44946	2.0592	1.9598
14.511	14.053	.53691	2.0629	1.9544
17.779	12.716	.59554	2.0641	1.9499
22.512	11.318	.67150	2.0647	1.9437
27.730	10.200	.74587	2.0617	1.9340
33.246	9.3166	.81715	2.0591	1.9258
39.342	8.5629	.88915	2.0560	1.9178
49.149	7.6506	.99305	2.0478	1.9027

The intercept on this plot corresponds to $K = 1.97_5 \times 10^{-5}$. The same value was derived from the familiar extrapolation[8] of log K' *vs.* $\sqrt{c_i}$, but with less precision.

The value 2.03×10^{-5} previously obtained by Ives, Linstead and Riley[13] differs from ours by about ten times the discrepancy to be expected from experimental errors alone, but is readily accounted for by differences in primary standards. The limiting conductances of the hydrogen and sodium ions which they employ[14] would tend to make their K about 1% larger than ours, and their cell constants are based upon data[15] which are higher than the generally accepted standard[5] by amounts ranging from a few tenths to several per cent., depending upon the concentration. In the light of these considerations there is little doubt that the present determination is the more reliable.

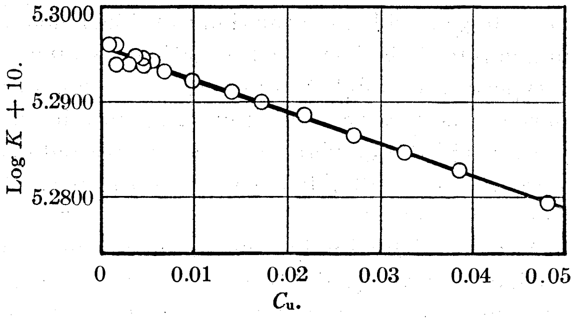

Fig. 1.

Summary

The equivalent conductances of α-crotonic acid and its sodium salt have been measured in dilute solution at 25°. The limiting equivalent conductance of sodium α-crotonate was found to be 83.30.

From these results, and data available in the literature, the value $K = 1.97_5 \times 10^{-5}$ was obtained for the thermodynamic ionization constant of α-crotonic acid at 25°.

NEW HAVEN, CONN. RECEIVED MARCH 23, 1937

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[11] *Cf.* Refs. 3 or 8 for details of calculations.

[12] An extended discussion of the extrapolation of dilution constants will appear in a communication by Saxton and Darken.

[13] Ives, Linstead and Riley, *J. Chem. Soc.*, 561 (1933).

[14] Ferguson and Vogel, *Phil. Mag.*, [4] **233**, 300 (1927); *cf.* MacInnes, Shedlovsky and Longworth, THIS JOURNAL, **54**, 2758 (1932) and ref. 3.

[15] Unpublished data of A. C. Melcher, Mass. Inst. Tech., 1912, quoted by Noyes and Falk, THIS JOURNAL, **34**, 454 (1912).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE CITY COLLEGE OF NEW YORK]

The Fatty Acids Associated with Banana Starch

BY LEO LEHRMAN AND ELVIN A. KABAT

It has already been shown that the starches of some of the common cereals (corn, rice and wheat)[1] and one of the tubers (cassava)[2] have fatty acids combined with carbohydrate in the α-amylose component. However, the amount in the latter starch is much smaller than in the former and also contains an additional fatty acid. Furthermore, another tuber (potato) starch does not contain any combined fatty acid.[3] Thus it is apparent that the combined fatty acids may vary in kind and amount with the type of starch. In order to gain added information as to the amount and nature of the fatty acids in different starches, a typical fruit starch was investigated. For this purpose the banana was selected, because in the green stage a large percentage of the dry pulp is starch. Specifically, bananas from the port of Limon were used.[4]

At first the dried pulp from the green fruit was used, but it was found that some naturally occurring substance made it very difficult to pulverize the residue, after drying, liberated by acid hydrolysis. As this is necessary in order to completely extract the fatty acids, the pure starch was made instead.[5] A total of about 3500 g. of starch was obtained starting with approximately 350 bananas.

In order to be sure that any fatty acids obtained were not originally present extraneously, all the starch was extracted with alcohol before carrying out the experimental work. Furthermore, to settle any question as to the presence of any glycerides as the source of the fatty material, the aqueous filtrate from the hydrolysis was analyzed for glycerol. As in previous investigations, the liberated fatty acids were examined also for other substances and phytosterol that might occur in the starch.

Experimental Part

Mixed Fatty Acids.—Extraction of a sample of the starch with petroleum ether for several hours showed a negligible amount of extractable material. Two separate portions of the starch weighing about 600 g. each were hydrolyzed with hydrochloric acid[1b] and the liberated fatty acids recovered by extraction with petroleum ether. This "fat by hydrolysis," a light yellow semi-solid, amounted to 0.2% in each case and had an iodine number of 59.4.[1a]

Examination of Filtrate for Glycerol.—Four liters of filtrate, reddish-brown in color, was evaporated on a steam-bath until a moist solid mass, black in color, was obtained. Alcohol was added, the mixture stirred well and filtered. The dark brown filtrate was again evaporated on the steam-bath to moist dryness. This process was repeated several times until a small amount of brown material, soluble in alcohol, resulted. A portion of this brown material gave a negative test for acrolein when heated with potassium bisulfate, indicating the absence of glycerol originally. Other tests[6] likewise showed the absence of glycerol.

Isolation and Identification of Saturated Fatty Acids.—In the separation of the saturated from the unsaturated fatty acids by the magnesium soap–alcohol method,[7] the insoluble magnesium soap was decomposed by heating with concentrated hydrochloric acid. The liberated fatty material, after several crystallizations from alcohol, was a white solid, melting point 62°. The phenylhydrazide was made[8] and had a melting point of 110°.[9]

The molecular weight of the acid was determined by titrating a weighed amount dissolved in alcohol with standardized sodium hydroxide using phenolphthalein as the indicator. Below are also given the results of micro carbon and hydrogen determinations.[10]

Anal. Calcd. for palmitic acid, $C_{16}H_{32}O_2$: C, 74.91; H, 12.59; mol. wt., 256.3. Found: C, 75.01; H, 12.16; mol. wt. (monobasic), 265.

The above data indicate the presence of palmitic acid in the mixed fatty acids.

Identification of Unsaturated Fatty Acids. A. By Oxidation.—The unsaturated fatty acids, separated from the saturated by the magnesium soap–alcohol method, was a light yellow oil having an iodine number of 147.1.

One and one-half grams was oxidized by potassium permanganate in alkaline solution.[11] The white solid oxidized acids were filtered, washed and allowed to dry. Then they were extracted with chloroform to effect a separation.[1b] On evaporation of the chloroform a fatty material was obtained which was re-oxidized and the resultant solid oxidized acids extracted with chloroform.

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[1] (a) Taylor and Lehrman, THIS JOURNAL, **48**, 1739 (1926); (b) Lehrman, *ibid.*, **51**, 2185 (1929); (c) **52**, 808 (1930).

[2] Lehrman, *ibid.*, **54**, 2527 (1932).

[3] Lehrman and Kabat, *ibid.*, **55**, 850 (1933).

[4] The authors wish to thank the United Fruit Co., Inc., New York City, for their kindness in supplying the necessary green bananas.

[5] The authors wish to thank the Corn Products Refining Co., Edgewater, N. J., for the use of their technical laboratory and the aid of their technical research staff in making the starch.

[6] (a) Denigès, *Bull. soc. pharm. Bord.*, **49**, 161 (1911); (b) Kolthoff, *Pharm. Weekblad.*, **61**, 1497 (1924).

[7] Thomas and Yu, THIS JOURNAL, **45**, 123 (1923).

[8] Brauns, *ibid.*, **42**, 1480 (1920).

[9] J. van Alphen, *Rec. trav. chim.*, **44**, 1064 (1925).

[10] The authors are indebted to Mr. William Saschek of the College of Physicians and Surgeons, Biochemical Department, for most of the analyses (micro) recorded in this paper.

[11] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," The Macmillan Company., New York, N. Y., 5th ed., Vol. I, p. 564.

The slight quantity of residues, insoluble in the chloroform extractions above, were combined and extracted with hot water. On cooling a small amount of white solid separated, which was crystallized from alcohol and water and had a melting point of 170–172°.

Anal. Calcd. for tetrahydroxystearic acid, $C_{18}H_{36}O_6$: C, 62.05; H, 10.34. Found: C, 61.95; H, 10.15.

Due to the small amount of material a molecular weight determination by titration could not be made.

The data indicate the presence of α-linoleic (linolic) acid,[12] in the unsaturated fatty acids.

The residue, obtained by the evaporation of the chloroform extracts, was extracted with petroleum ether to remove unoxidized fatty material. It was then extracted with ether in order to make a separation. The residue, insoluble in ether, was crystallized from alcohol and water, yielding a white solid, melting point 154–155°.

Anal. Calcd. for tetrahydroxystearic acid, $C_{18}H_{36}O_6$: C, 62.05; H, 10.34; mol. wt., 348. Found: C, 62.00; H, 9.95; mol. wt. (monobasic), 354.

The above data are added evidence of the presence of α-linoleic (linolic) acid[12] in the unsaturated fatty acids.

The ether extract was allowed to evaporate and the residue crystallized several times from alcohol. It was a white solid, melting point 115–117°.

Anal. Calcd. for dihydroxystearic acid, $C_{18}H_{36}O_4$: C, 68.35; H, 11.39; mol. wt., 316. Found: C, 68.00; H, 11.22; mol. wt. (monobasic), 319.

The data indicate the presence of oleic acid in the unsaturated fatty acids.

The water filtrates from the two oxidations were combined and examined for higher hydroxy acids,[11] with negative results. This indicates the possible absence[2] of acids more unsaturated than linoleic (linolic) in the unsaturated fatty acids.

B. Bromination.—One gram of the unsaturated fatty acids was brominated[13] yielding a small amount of white precipitate in the cold petroleum ether. This precipitate, together with a small amount of similar material recovered from the evaporated petroleum ether filtrate (see below), was extracted with hot petroleum ether. After evaporation of the petroleum ether, the residue was crystallized from ether yielding a white solid, melting point 176.5–177°.

Anal. (Carius) Calcd. for hexabromostearic acid, $C_{18}H_{30}O_2Br_6$: Br, 63.34. Found: Br, 63.55.

The data indicate the presence of linolenic acid in the unsaturated fatty acids. Additional qualitative tests for linolenic acid were obtained in both the mixed and unsaturated fatty acids using arsenotungstic acid.[14] It is interesting to note the detection of this acid by its bromide and the failure to find its oxidized product, hexahydroxystearic acid. This result is similar to that found previously by the first author with linolenic acid from cassava starch.[2] This further confirms his conclusion that bromination is a more delicate method for detecting small amounts of linolenic acid than oxidation.

The petroleum ether filtrate was allowed to evaporate and the residue treated with ether. A small amount of white solid did not dissolve. As the melting point indicated the presence of the hexabromo compound, it was combined with the material insoluble in the cold petroleum ether (see above). The ether was allowed to evaporate and the residue recrystallized first from ether and finally from petroleum ether. It was a white solid, melting point 113°.

Anal. (Carius) Calcd. for tetrabromostearic acid, $C_{18}H_{32}O_2Br_4$: Br, 53.33. Found: Br, 53.00.

These data are added evidence for the presence of α-linoleic (linolic) acid in the unsaturated fatty acids.

Examination for Other Substances.—Tests on the resultant solution from a sodium fusion with a portion of the mixed fatty acids showed the absence of nitrogen, sulfur and halogens. Results obtained from the fusion of another portion of the mixed fatty acids with a mixture of equal parts of sodium carbonate and sodium nitrate indicated the absence of phosphorus.

The mixed fatty acids were tested for phytosterol by the Liebermann–Burchard reaction[11] (p. 270) and the precipitation with 1% alcoholic digitonin,[11] (p. 264) both being positive. The precipitate of the latter, after washing and drying, was silky white platelets having a melting point of 208–212°. However, there was too small an amount to obtain any added data. An attempt was made to isolate enough of the pure phytosterol,[15] for further identification, from a portion of the mixed fatty acids, but the amount again was too small to work with. In order to ascertain whether or not the phytosterol could have its source in some extraneous material, the alcohol used for the extraction of the starch was evaporated to dryness. The residue was then subjected to the same tests with negative results. As a further check 500 g. of alcohol extracted starch was extracted with petroleum ether. After evaporation of the petroleum ether a very small residue was obtained in which the absence of phytosterol was shown by the same tests.

Summary

The amount of fatty acids liberated by the hydrolysis of banana starch free from extraneous fatty material has been determined to be 0.2%.

The fatty acids have been found to consist of a mixture of palmitic, oleic, linoleic (linolic) and linolenic acids together with a very small amount of phytosterol.

The detection of small amounts of linolenic acid in the presence of oleic and linoleic (linolic) by bromination has again been shown to be a more sensitive method than oxidation.

This is the first time that phytosterol has been found combined in a starch.

NEW YORK, N. Y. RECEIVED MARCH 29, 1937

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(12) Green and Hilditch, *Biochem. J.*, **29**, 1552–63 (1935).

(13) Maksimov, *Bull. Far Eastern Branch Acad. Sci. U. S. S. R.*, 99–102 (1934).

(14) Martin, THIS JOURNAL, **58**, 364 (1936).

(15) Hertwig, Jamieson, Baughman and Bailey, *J. Assoc. Off. Agr. Chem.*, **8**, 439–42 (1925).

[CONTRIBUTION FROM RESEARCH LABORATORY, MERCK & COMPANY, INC., AND PRIVATE LABORATORIES]

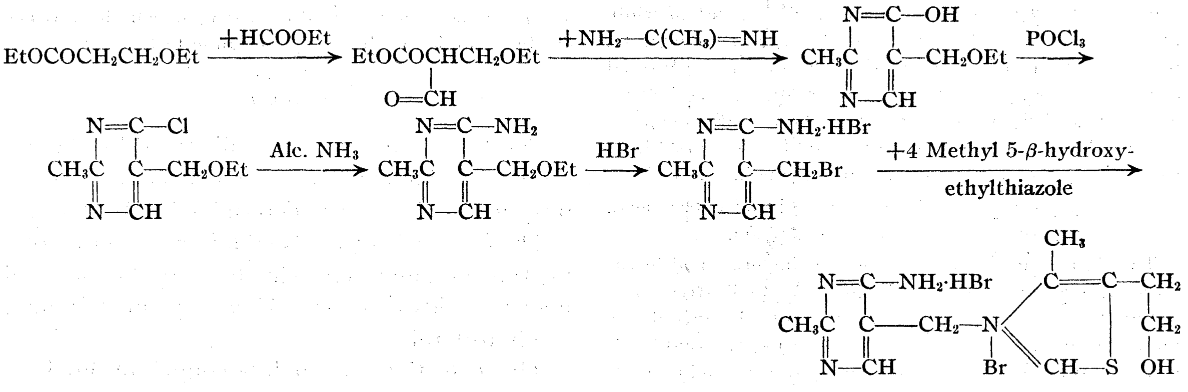
Studies of Crystalline Vitamin B_1. XVII. Synthesis of Vitamin B_1

BY JOSEPH K. CLINE, ROBERT R. WILLIAMS AND JACOB FINKELSTEIN

The structure of vitamin B_1 having been determined by previous identification and ultimate synthesis of several degradation products, notably 4-methyl-5-beta-hydroxyethylthiazole,[1] 2,5-dimethyl-6-aminopyrimidine,[2] 2-methyl-6-oxypyrimidine-5-methylene sulfonic acid[3] and the mode of linkage of the two nuclei indicated by the presence of quaternary nitrogen in the vitamin,[4] a synthesis of the vitamin was undertaken.

The possibilities of three principal routes of synthesis leading to the pyrimidine portion of the vitamin were explored: (1) the addition of formaldehyde to the 5-position of an appropriate pyrimidine; (2) a Curtius, Hoffmann or Loessen degradation of appropriate derivatives of 2-methyl-6-oxypyrimidine-5-acetic acid whose ethyl ester, hydrazide and amide we had prepared in excellent yields; and (3) the conversion of a 5-ethyoxymethyl-pyrimidine into the corresponding 5-halomethyl derivative.

Of these the first two proved difficult to control at one or more stages. The third offered more promise of amenability. As has been indicated in a preliminary communication,[5] a successful synthesis has been worked out according to the scheme



The final condensation step in the synthesis took place less readily than had been anticipated and numerous trials were necessary before crystalline material was obtained in a state of apparent purity although ample antineuritic potency could be demonstrated in the reaction mixtures by physiological tests. The difficulty of isolating the crystals was enhanced by their surprising solubility in alcoholic solvents. As first obtained, the crystalline bromide hydrobromide melted at 219–220° and the chloride hydrochloride at 232–234°. These were obtained by adding ether to methanol solutions. Presently, however, through the cooperation of Dr. A. G. Stein, a method was evolved whereby the vitamin was recrystallized as the bromide hydrobromide from methanol and as the chloride hydrochloride from water and ethanol. The bromide hydrobromide so obtained melted at 227–231° and the chloride hydrochloride at 248–250°. In no case is the melting point of either natural or synthetic vitamin very satisfactory as a criterion of purity as melting is preceded by decomposition. Further, melting on a hot stage under crossed Nicols reveals that in all cases a loss of birefringence occurs at about 190°, suggesting some intramolecular transformation at that temperature.

We have compared the low and high melting forms somewhat elaborately by crystallographic, spectrometric and electrometric means as well as analytically without detecting clear evidence of the presence of an impurity in the low melting crystals. Furthermore, numerous physiological tests including both curative and prophylactic experiments have likewise indicated as yet no significant deviations among the two forms of synthetic and the natural chloride. Further re-

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(1) H. T. Clarke and S. Gurin, THIS JOURNAL, **57**, 1876 (1935); E. R. Buchman, *ibid.*, **58**, 1803–1805 (1936).

(2) R. R. Williams, A. E. Ruehle and J. Finkelstein, *ibid.*, **59**, 526–530 (1937).

(3) J. K. Cline, R. R. Williams, A. E. Ruehle and R. E. Waterman, *ibid.*, **59**, 530–533 (1937).

(4) R. R. Williams and A. E. Ruehle, *ibid.*, **57**, 1856–1860 (1935).

(5) R. R. Williams, *ibid.*, **58**, 1063–1064 (1936).

port will be made when these experiments are complete.[6]

Immediately after the publication of our preliminary communication of the synthesis,[7] there reached us a paper by Dr. Rudolf Grewe[8] confirming the structure previously proposed by ourselves[5] and containing the information that a synthesis of the vitamin had been achieved in recent months by Drs. Andersag and Westphal at the Elberfeld Laboratories of the I. G. Farbenindustrie A.-G. To date no publication has appeared revealing the route of this synthesis or the characteristics of the product. It is therefore impossible to compare the results with our own at this time. Happily, however, for science there appears to be no ground for dispute regarding the true constitution of the vitamin.

The yields reported herein have in many instances been improved by modifications which are still under investigation. Our synthesis has proved amenable to large scale development and has already been utilized for the production of many kilos of the vitamin on an economical basis.

Ethyl Sodioformyl-β-ethoxypropionate.—A mixture of 73 g. of ethyl β-ethoxypropionate and 40 g. of ethyl formate was dropped slowly during eight hours onto 12 g. of sodium wire covered with anhydrous ether. The yellow sodioformyl derivative thus formed appeared as a solid mass which occluded all the ether and unreacted esters. The sodioformyl derivative was used without isolation for the subsequent reaction. It must be protected from atmospheric moisture and should be used promptly as it is not very stable.

2-Methyl-5-ethoxymethyl-6-oxypyrimidine.—To the crude sodioformyl derivative obtained above 45 g. of acetamidine hydrochloride, 100 cc. of absolute alcohol, and a solution of 12 g. of sodium in 200 cc. of absolute alcohol were added. The ether was distilled off and the mixture heated, under reflux, for sixteen hours. The contents of the flask was then cooled, neutralized with 10% acetic acid and evaporated on the steam-bath. The residue was taken up in a small amount of water and extracted repeatedly with chloroform. The combined chloroform extracts were dried over anhydrous sodium sulfate and the chloroform removed by evaporation *in vacuo*. The remaining brown gummy substance was treated with dioxane, which dissolved a portion and left a discolored white solid. The residual solid was separated, dried, and sublimed in high vacuum at 140°. The sublimate was placed in a Soxhlet extractor, extracted repeatedly with anhydrous ether and the residue again sublimed in high vacuum. The sublimate was a pure white cake of 2-methyl-5-ethoxymethyl-6-oxypyrimidine which melted at 175–176°; yield 3.5%.

Anal. Calcd. for $C_8H_{12}O_2N_2$: C, 57.11; H, 7.20. Found: C, 56.92, 56.96; H, 7.04, 6.84.

2-Methyl-5-ethoxymethyl-6-chloropyrimidine.—One gram of 2-methyl-5-ethoxymethyl-6-oxypyrimidine was heated with 8 cc. of phosphorus oxychloride for three hours at 78°. The pyrimidine dissolved slowly and left but a small quantity of undissolved material. The excess phosphorus oxychloride was then distilled off *in vacuo*. To the residue was added a small amount of crushed ice and water and the excess acid neutralized by the addition of solid sodium bicarbonate. The dark colored solution was extracted repeatedly with chloroform and the combined chloroform extracts were dried over anhydrous sodium sulfate. The chloroform was removed *in vacuo* and the residue distilled. A fraction which boiled at 78–80° at 1 mm. was collected. On redistillation the pure chloropyrimidine boiled at 72–73° at 0.5 mm. and was obtained as a colorless oil with an odor resembling acetamide; yield 70%.

Anal. Calcd. for $C_8H_{11}N_2OCl$: C, 51.46; H, 5.94; N, 15.01; Cl, 19.01. Found: C, 50.84, 50.82; H, 5.64, 5.70; N, 14.85, 14.92; Cl, 18.95.

2-Methyl-5-ethoxymethyl-6-aminopyrimidine.—One gram of 2-methyl-5-ethoxymethyl-6-chloropyrimidine was treated with 15 cc. of saturated alcoholic ammonia in a bomb-tube at 140° for fifteen hours. The contents of the tube were concentrated *in vacuo* and a partly crystalline residue remained. The residue was dissolved in a small amount of water, the solution made alkaline by addition of sodium carbonate and the solution then extracted repeatedly with chloroform. The combined chloroform extracts were dried over anhydrous sodium sulfate and the chloroform was removed *in vacuo*. A gummy residue containing a small amount of crystals was left. When this residue was treated with hot anhydrous ether a solid separated immediately. The solid was removed by centrifuging and discarded. The ethereal mother liquors on standing and partial evaporation of the ether deposited large crystals of the impure aminopyrimidine, which were filtered off, dried, and purified by repeated sublimation in high vacuum at 60–80°. The product, a pure white pyrimidine with an odor reminiscent of piperidine, melted at 89.5–90.5°; yield 70%. *Anal.* Calcd. for $C_8H_{13}ON_3$: C, 57.45; H, 7.58; N, 25.13. Found: C, 57.31, 57.62; H, 7.62, 7.65; N, 25.64, 25.50, 25.82.

2-Methyl-5-bromomethyl-6-aminopyrimidine Hydrobromide.—One hundred and fifty mg. of 2-methyl-5-ethoxymethyl-6-aminopyrimidine was heated with 10 cc. of a 10% solution of anhydrous hydrobromic acid in glacial acetic acid for two hours at 100°. At the end of this time the mixture was cooled and the liquid remaining decanted from the crystals which separated out. The crystals were washed several times with anhydrous ether and then purified by dissolving in a small amount of cold methanol and reprecipitating by the addition of ether. The pure compound as obtained melts at 192–193° and is the hydrobromide of 2-methyl-5-bromomethyl-6-aminopyrimidine; yield 90%. *Anal.* Calcd. for $C_6H_9N_3Br_2$: C, 25.45; H, 3.21; N, 14.85. Found: C, 26.36, 26.55, 26.45; H, 3.50, 3.62, 3.34; N, 14.71, 14.99.

Vitamin B1 Bromide Hydrobromide.—One hundred and fifty mg. of 2-methyl-5-bromomethyl-6-aminopyrimidine hydrobromide was heated with 150 mg. of 4-methyl-5-β-

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(6) R. R. Williams and J. K. Cline, THIS JOURNAL, **59**, 216 (1937).

(7) R. R. Williams and J. K. Cline, *ibid.*, **58**, 1504–1505 (1936).

(8) R. Grewe, *Z. physiol. Chem.*, **242**, 89–96 (1936).

hydroxyethylthiazole[9] and 0.2 cc. of butanol for fifteen minutes at 120°. The pyrimidine went into solution and shortly thereafter a precipitate settled out. The reaction mixture was diluted with 1 cc. of boiling absolute ethyl alcohol and allowed to stand until no more material settled out. The alcoholic mother liquors were removed by filtration and the precipitate washed several times with small amounts of cold absolute ethyl alcohol. The precipitate then was recrystallized by dissolving in hot methanol, adding absolute alcohol to the hot solution until a permanent cloud appeared and allowing to cool slowly.

The condensation product thus obtained occurs as rosets of needles which melt at 229–231°; yield 45%.

With doses of 6 γ, cures of polyneuritis were effected in rats on a vitamin B_1-free diet. These cures endured for several days, indicating an activity equal to the natural vitamin. It appears to hold one-half molecule of water of crystallization. *Anal.* Calcd. for $C_{12}H_{17}ON_4SBr \cdot HBr \cdot 0.5\,H_2O$: C, 33.09, H, 4.51; N, 12.87. Found: C, 33.18, 32.76; H, 4.82, 4.70; N, 12.73.

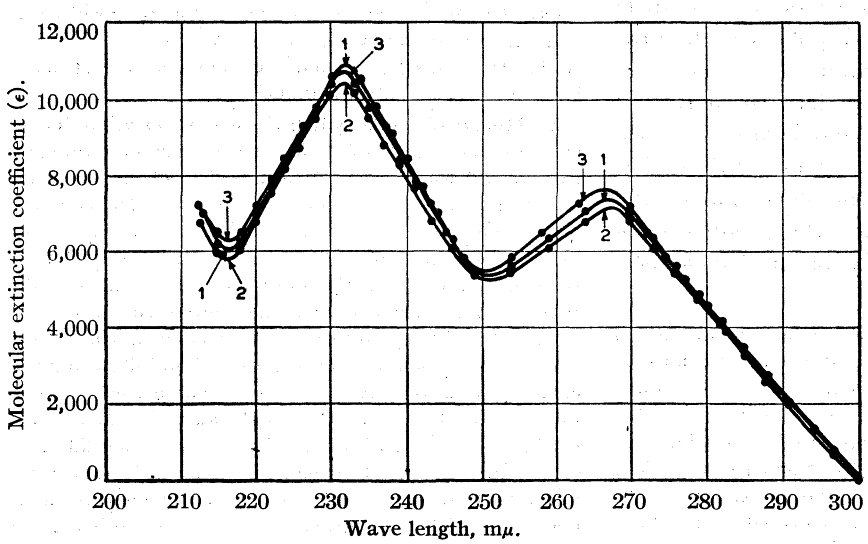

Fig. 1.—Curve 1, natural vitamin (hydrochloride); curve 2, synthetic vitamin (hydrochloride); curve 3, synthetic vitamin (hydrobromide).

Vitamin B_1 Chloride Hydrochloride.—One hundred and fifty mg. of vitamin B_1 bromide hydrobromide was dissolved in hot methanol and shaken with slight excess silver chloride for a half hour.

The silver salts were filtered off and to the hot solution absolute alcohol was added to incipient cloudiness. On cooling the vitamin hydrochloride crystallized out. To free it from traces of silver chloride it was dissolved in a little water and filtered. The filtrate was evaporated *in vacuo* to dryness, the crystalline residue was dissolved in a minimum amount of water and to the hot aqueous solution ten volumes of absolute alcohol was added. On standing the crystalline chloride hydrochloride separated melting at 248–250°; yield 90%. *Anal.* Calcd. for $C_{12}H_{17}ON_4SCl \cdot HCl \cdot 0.5H_2O$: C, 41.60; H, 5.53; N, 16.17; Cl,[10] 21.04; S,[10] 9.51. Found: C, 41.30, 41.72; H, 5.48, 5.64; N, 16.25, 16.26; Cl,[10] 21.30, 21.13; S,[10] 9.72, 9.56.

A comparison of the ultraviolet absorptions of the natural and synthetic products is shown in Fig. 1. Curative tests on polyneuritic rats have given the following results:

No. rats	Dose in γ	Cured	Recurrence of polyneuritis, days
7	3	2	6
7	4	2	5.5
7	4.5	3	6.7
12	5	7	6.3
8	5.5	7	7
9	6.0	9	5.6

We gratefully acknowledge our indebtedness to Mr. D. F. Hayman and Mr. S. Adler for the microanalyses, to Mr. A. E. Ruehle for the spectrograms, to Dr. E. R. Buchman for several samples of 4-methyl-5-β-hydroxyethylthiazole, and to Mr. H. W. Hermance for the crystallographic comparison of the synthetic and natural vitamin. Thanks are also due to Dr. R. T. Major for advice and for facilities put at our disposal. We also wish to express our appreciation to Dr. Hans Molitor and Mr. W. L. Sampson for the many physiological assays necessary in the course of the work.

Summary

1. A practical synthesis of vitamin B_1 has been described.

2. The synthesis of several new pyrimidines useful as intermediates in the synthesis of vitamin B_1 has been described.

3. The structure previously proposed for vitamin B_1 has been confirmed by synthesis.

RAHWAY, NEW JERSEY RECEIVED APRIL 7, 1937

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[9] E. R. Buchman, THIS JOURNAL, **58**, 1803 (1936).

[10] Analyses performed on anhydrous vitamin on macro scale. On account of hygroscopicity of the vitamin, Cl and S determinations on a micro scale were not very satisfactory. See Wintersteiner, Williams and Ruehle, THIS JOURNAL, **57**, 517 (1935).

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

The Decomposition of 2-Fluorenediazonium Chloride and 2-Fluorenonediazonium Chloride in Acetic Acid

BY H. V. CLABORN AND H. L. HALLER

In preparing derivatives of fluorene to be tested for their insecticidal action, it became desirable to prepare 2-acetoxyfluorene and 2-acetoxyfluorenone. These compounds are not described in the literature, but it was found that they could be obtained readily by the acetylation of the corresponding hydroxy compounds. The latter compounds were first prepared by Diels,[1] who obtained them by the decomposition of the corresponding diazonium chlorides with water in the usual manner. The yield of the 2-hydroxyfluorene was reported to vary considerably, and this observation has been confirmed by us. When, however, the decomposition of the diazonium chloride was carried out in 3% sulfuric acid, as suggested by Ruiz,[2] an 80% yield of the 2-hydroxyfluorene was obtained.

The decomposition of 2-fluorenonediazonium chloride in water gave 2-hydroxyfluorenone in a yield of 55%, whereas in dilute acetic acid, as suggested by Patrizietti,[3] an 80% yield of the same compound was obtained.

The replacement of the amino group by the acetoxy group through the diazo reaction has been accomplished by the decomposition of a dry diazonitrate or sulfate with glacial acetic acid;[4] by the interaction of a diazo bromide and acetic anhydride;[5] by the diazotization of an amine in glacial acetic acid;[6] and more recently by the interaction of solid aryl diazonium borofluorides and acetic acid.[7,8] In the last reaction the acetates of phenols are obtained in good yield, and this reaction is particularly useful when the normal decomposition does not take place readily. Since 2-fluorenediazonium chloride and 2-fluorenonediazonium chloride are fairly stable solids, it seemed of interest to attempt the preparation of the acetoxy compounds directly from the diazonium chlorides and acetic acid. When the experiment was carried out with 2-fluorenediazonium chloride, three compounds were obtained, with the following yields: 2-chlorofluorene, 10%; 2-acetoxyfluorene, 46.7%; and 2-hydroxyfluorene, 11%. The last-named compound separated readily from the reaction mixture by extraction with alkali. Although a partial separation of the chloro and the acetoxyfluorenes could be effected by recrystallization from methanol, it was found expedient to separate the two by saponifying the acetate with alkali to the phenol and removing the chloro compound by filtration from the alkaline solution.

The interaction of 2-fluorenonediazonium chloride and acetic acid gave a 60% yield of 2-acetoxyfluorenone.

Experimental

Interaction of 2-Fluorenediazonium Chloride and Acetic Acid.—A solution of 10 g. of 2-fluorenediazonium chloride in 50 cc. of glacial acetic acid was heated gently under a reflux condenser until nitrogen began to be evolved. After the vigorous reaction had subsided, the solution was boiled for five minutes and then concentrated under reduced pressure until most of the acetic acid was removed. The concentrated solution was poured into ice water; the separated product was removed by filtration and dried; yield 7.6 g.; m. p. 85–100°. The product was dissolved in ether and extracted twice with 5% potassium hydroxide solution. The combined alkaline solutions were acidified with dilute hydrochloric acid, and the precipitated phenol was separated by filtration. It was recrystallized from 50% acetic acid; yield 1.1 g.; m. p. 168°. When mixed with an equal quantity of authentic 2-fluorenol, there was no depression of the melting point.

From the ether solution there was obtained, after drying over sodium sulfate and removal of the ether, 5.8 g. of a mixture of the chlorofluorene and acetoxyfluorene. This mixture was best separated by heating it to boiling for thirty minutes with 30 cc. of 10% potassium hydroxide solution, cooling, and then removing the chloro compound by filtration. The chloro compound was then purified by steam distillation; yield 1 g.; m. p. 168°. It was identified as 2-chlorofluorene by a mixed melting point determination with authentic material prepared according to the method of Chanussot.[9]

2-Acetoxyfluorene.—One gram of 2-fluorenol was refluxed for thirty minutes with 5 cc. of acetic anhydride and 0.5 g. of anhydrous sodium acetate. The solution was cooled and a small volume of methanol added to decompose the acetic anhydride. The solution was poured slowly, with stirring, into ice water. The acetate sepa-

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(1) O. Diels, *Ber.*, **34**, 1758 (1901).

(2) C. Ruiz, *Anal. asoc. quím. argentina*, **16**, 170 (1928).

(3) R. Patrizietti, *ibid.*, **22**, 24 (1934).

(4) W. R. Orndorff, *Am. Chem. J.*, **10**, 368 (1888).

(5) O. Wallach, *Ann.*, **235**, 233 (1886).

(6) R. Mendola and F. J. East, *J. Chem. Soc.*, **53**, 460 (1888).

(7) H. L. Haller and P. S. Schaffer, THIS JOURNAL, **55**, 4954 (1933).

(8) L. E. Smith and H. L. Haller, *ibid.*, **56**, 237 (1934).

(9) P. Chanussot, *Anal. asoc. quím. argentina*, **15**, 216 (1927).

rated as colorless crystals, which were removed by filtration. These were washed with water and dried; yield 1.1 g. After recrystallization from dilute methanol the compound melted at 128°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.32; H, 5.40. Found: C, 80.16; H, 5.46.

2-Acetoxyfluorenone.—One gram of 2-fluorenonediazonium chloride in 5 cc. of glacial acetic acid was heated gently until the evolution of nitrogen began. After the initial reaction subsided, the solution was again heated carefully until the evolution of nitrogen ceased and then boiled for five minutes. Fifteen cubic centimeters of ethanol was then added and the solution chilled in ice. The product which separated consisted of large yellow plates; yield 0.6 g.; m. p. 154°. After recrystallization from 95% ethanol, it melted at 157°. The compound was identified as 2-acetoxyfluorenone by a mixed melting point determination with an authentic sample of 2-acetoxyfluorenone. The latter was obtained by acetylation of 2-hydroxyfluorenone (1 g.) according to the method described for the preparation of 2-acetoxyfluorene. The yield was 1.15 g. On recrystallization from 95% ethanol it melted at 157°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.60; H, 4.23. Found: C, 75.43; H, 4.28.

On saponification with 5% potassium hydroxide solution 2-acetoxyfluorenone (1.9 g.) was converted into 2-hydroxyfluorenone (1.5 g.), which after recrystallization from 50% acetic acid melted at 204°. Diels[1] reports this compound as sintering at 200° and melting at 206.7°.

Summary

The interaction of 2-fluorenediazonium chloride and acetic acid gives three compounds in the following yields: 2-chlorofluorene, 10%; 2-acetoxyfluorene, 46.7%; and 2-hydroxyfluorene, 11%.

From 2-fluorenonediazonium chloride and acetic acid there was obtained a 60% yield of 2-acetoxyfluorenone.

Washington, D. C. Received March 20, 1937

[Contribution from the Research Laboratories of the Universal Oil Products Company]

Identification of Alkylbenzenes. I. Identification of Monoalkylbenzenes by Means of the Acetamino Derivative[1]

By V. N. Ipatieff and Louis Schmerling

In the course of the study of the alkylation,[2] depolyalkylation,[3] and destructive alkylation[4] of aromatic hydrocarbons, the need for a simple method for the identification of alkylbenzenes became apparent. The boiling points and other physical constants are fairly satisfactory for distinguishing the homologous compounds but are inadequate in the case of isomers. Oxidation to benzoic acid or to one of the phthalic acids may be used to differentiate between mono- and dialkylbenzenes but is of no aid in the determination of the structure of the alkyl groups.

In the present investigation, the characterization of monoalkylbenzenes by means of their mono- and diacetamino derivatives was studied. Although there was nothing inherently new in the preparation of such derivatives by nitration, followed by reduction of the nitro compound and subsequent acetylation of the amine, there had been no previous study of the nitration of a series of alkylbenzenes under a single set of conditions; furthermore, it was not possible to predict whether the solid derivative would be a single compound or a mixture. If the nitration yielded a mixture of ortho and para isomers, the reaction would not be applicable. On the other hand, the preparation of a dinitro derivative would eliminate this difficulty since there is ample evidence[5] to show that only the 2,4-dinitro compound would be obtained.

The problem, then, consisted essentially in determining the conditions necessary for the formation either of a mononitro derivative, unadmixed with isomers, or of the dinitro derivative. This was less difficult than had been anticipated, and a procedure was developed by means of which monoalkylbenzenes may be identified easily and quickly using small amounts of material. It was found that under the prescribed conditions pure 4-nitroalkylbenzenes may be obtained by use of a nitrating mixture consisting of equal volumes of concentrated nitric and sulfuric acids. The ortho-substituted isomers are present in such small amount, if at all, that they do not interfere. It

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(1) Presented before the Division of Organic Chemistry at the Chapel Hill meeting of the American Chemical Society, April, 1937.

(2) Ipatieff, Corson and Pines, This Journal, **58**, 919 (1936).

(3) Ipatieff and Pines, *ibid.*, **58**, 1056 (1936).

(4) Grosse and Ipatieff, *ibid.*, **57**, 2415 (1935); Ipatieff, Komarewsky and Pines, *ibid.*, **58**, 918 (1936).

(5) Shoesmith and Mackie, *J. Chem. Soc.*, 2334 (1928); Brady and Cunningham, *ibid.*, 121 (1934).

was found further that by use of more vigorous nitrating solution (namely, one composed of two volumes of sulfuric acid to one of nitric acid) it is the 2,4-dinitroalkylbenzenes[6] which are formed.

It is thus possible to obtain either the 4-acetamino- or the 2,4-diacetaminoalkylbenzenes as desired. The first are more suitable in the characterization of pure hydrocarbons; the second, because of solubility and other physical properties, in the identification of the components of aromatic mixtures. An important application of the latter consists of distinguishing between *n*- and isopropylbenzene when they occur separately or in a mixture with each other. Such an analysis is, of course, very desirable since the boiling points of the hydrocarbons are too close together to permit of their separation or definite identification. Although their diacetamino derivatives melt only 8° apart, there is little danger of confusing the derivatives since they crystallize in markedly different form and can be distinguished easily with the aid of a polarizing microscope.

In some cases, the mononitro compound may be contaminated with a small amount of the dinitrated hydrocarbon, and *vice versa*. Fortunately, the two may readily be separated by means of an ether extraction of the solution obtained on reducing the compounds with tin and hydrochloric acid. The monoamino compound forms an ether-soluble salt (presumably, $2RC_6H_4NH_2 \cdot SnCl_2 \cdot 2HCl$) with tin chloride in the presence of hydrogen chloride, whereas the analogous salt of the diaminoalkylbenzene is ether-insoluble. The material obtained from the ether extract is worked up separately from the other, and both the mono- and the diacetaminoalkylbenzenes may thus be obtained in a pure state from a single nitration product, giving a check on the identity of the hydrocarbon.

This method has been applied successfully by us in the determination of the structure of the different amylbenzenes obtained by the alkylation of benzene with cyclopentane and with methylcyclobutane, full details of which will be given in a forthcoming publication by Grosse and Ipatieff.

Experimental

Procedure.—A mixture of 0.5–1.0 cc. of the aromatic hydrocarbon and 5 cc. of a nitrating mixture was shaken for three to five minutes. The nitrating mixture consisted of equal volumes of sulfuric acid (d. 1.84) and nitric acid (d. 1.42), when the mononitro compound was desired as the chief product (Note 1), or of two volumes of the sulfuric acid to one of the nitric when it was the disubstituted derivative which was to be obtained. No attempt was made to cool the reaction mixture. When the evolution of heat had ceased, the mixture was poured upon a small amount of cracked ice; the oily nitro layer was taken up in ether, washed twice with water, and the ether was evaporated on a water-bath. To the residue was added 5 g. of granulated tin, 5 cc. of concentrated hydrochloric acid, and sufficient ethyl alcohol to bring all, or nearly all, of the nitrocompound into solution. The mixture was shaken until reduction was complete as was shown by the absence of marked turbidity on pouring a test portion into water (Note 2). This usually required less than ten minutes. In those cases in which the reduction took place more slowly, the reaction was hastened by heating the mixture on the water-bath; usually, however, the reduction was very exothermic and did not require the application of external heat. When reduction was complete, the aqueous alcoholic solution was decanted from the excess tin into about 20 cc. of water. The solution was extracted with ether and sufficient concentrated alkali was added to the aqueous solution to dissolve most of the precipitate of tin hydroxide which formed at first. The amino compound was extracted with ether, washed with water, dried by shaking for a few minutes with potassium carbonate, and the ether removed by evaporation. To the residue there was added 1 cc. of acetic anhydride. The derivative usually crystallized almost immediately. The material was warmed with 5 cc. of water to hydrolyze the excess anhydride. Since some of the acetamino derivatives are quite soluble in dilute acetic acid, it was occasionally necessary to evaporate almost to

100 ×.

Fig. 1.—Mixture of the diacetamino derivatives of *n*- and isopropylbenzene.

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[6] The orientation of the nitro groups has been proved for toluene, ethylbenzene, *n*-propylbenzene, and *t*-butylbenzene (*cf.* references in preceding footnote). It is presumably the same in the case of all the disubstituted monoalkylbenzenes prepared by the procedure described in this paper.

dryness the aqueous solution containing the hydrolyzed acetic anhydride. The crude derivative was filtered and then recrystallized from hot water or dilute alcohol, yield 40–70%.

The ether extract of the reduction solution was tested in order to determine whether it consisted of traces of unreduced nitro compound or of an amine–tin chloride complex. In the latter case the amine was liberated by the addition of alkali and worked up separately from the main batch of derivative. Although the amount of material thus received was often only a small portion of the total, this was well worthwhile since it was the monoacetaminoalkylbenzene only which was obtained, even when the derivative prepared from the major portion was the diacetamino compound. When the chief or only product was the monosubstituted derivative, two alternatives were possible: either part of the compound could be obtained from the ether extract and the remainder from the aqueous solution, or the ether extraction could be made complete and all the monoamine isolated therefrom. The latter procedure gave the more satisfactory results, especially when small amounts of diaminoalkylbenzene were present.

The time required for the preparation of the derivative, exclusive of the recrystallization of the product, was about thirty minutes.

NOTE 1.—Both toluene and ethylbenzene yielded practically only the 2,4-dinitroalkylbenzene regardless of which nitrating mixture was used. For neither hydrocarbon could more than traces of the monosubstituted derivative be isolated. The *n*-alkylbenzenes showed a marked tendency to yield dinitro derivatives even with the milder nitrating solution. In the case of *n*-propylbenzene and of *n*-butylbenzene the formation of the dinitrated by-product could be greatly diminished by cooling the reaction mixture.

TABLE I

p-$RC_6H_4NHCOCH_3$

Mixed m. p. (1:1 mixture) of *n*-C_3H_7 with iso-C_3H_7, 90–92°. Mixed m. p. of *i*-C_3H_7 with *n*-C_4H_9, 83–87°. Mixed m. p. of *s*-C_4H_9 with cyc-C_6H_{11}, 109–111°.

R =	M. p., °C. (uncorr.)	Crystalline form (macroscopic appearance)
CH_3[c]	(145)[e]	
C_2H_5[c]	(94)[f]	
n-C_3H_7[a]	96[g]	Pearly flakes
i-C_3H_7[b]	106[h]	Glistening flakes
n-C_4H_9[c]	105[i]	Pearly flakes
s-C_4H_9[b]	126[j]	Pearly flakes
t-C_4H_9[b]	170[k]	Pearly flakes
t-C_5H_{11}[b]	142[l]	Pearly flakes
cyc-C_6H_{11}[d]	130–131[m]	Glistening flakes

[a] Prepared by the hydrogenation of allylbenzene. [b] Prepared by the method of Ipatieff, Corson and Pines [THIS JOURNAL, **58,** 919 (1936)]. [c] Eastman product, purified and redistilled. [d] Prepared by the method of Corson and Ipatieff [THIS JOURNAL, **59,** 645 (1937)]. [e] Beilstein, 4th ed., Vol. XII, p. 920. This derivative is not usually obtained by this method. [f] *Ibid.*, p. 1090. This derivative is not usually obtained by this method. [g] Baddely and Kenner [*J. Chem. Soc.*, 307 (1935)] also report 96°; previous workers, 87°. [h] Constam and Goldschmidt [*Ber.*, **21,** 1159 (1888)] report 102–102.5°. [i] Reilly and Hickinbottom, *J. Chem. Soc.*, **117,** 111 (1920). [j] *Idem.*, p. 120. [k] Beilstein, 4th ed., Vol. XII, p. 1167; *cf.* Shoesmith and Mackie, *J. Chem. Soc.*, 2335 (1928). [l] Anschütz and Beckerhoff [*Ann.*, **327,** 222 (1903)] report 138–139°. [m] Kurssanov [*ibid.*, **318,** 324 (1901)] reports 128–129.5°.

TABLE II

$RC_6H_3(NHCOCH_3)_2$

Mixed m. p. of CH_3 with C_2H_5, 190–195°. Mixed m. p. of *n*-C_3H_7 with *i*-C_3H_7, 197–200°. Mixed m. p. of *i*-C_3H_7 with *n*-C_4H_9, 187–190°. Mixed m. p. of *n*-C_3H_7 with *t*-C_4H_9, 185–189°. Mixed m. p. of *n*-C_4H_9 with *t*-C_4H_9, 180–185°.

R =	M. p., °C. (uncorr.)	Crystalline form (microscopic appearance)	Nitrogen, % Calcd.	Nitrogen, % Found
CH_3	221[a]	Small needles		
C_2H_5	223[b]	Small needles		
n-C_3H_7	208	Small feathery needles	11.96	11.73
iso-C_3H_7	216	Six-sided prisms	11.96	11.92
n-C_4H_9	214	Soft white needles	11.29	11.19
s-C_4H_9	192	Stout needles	11.29	11.03
t-C_4H_9	210	Rectangular prisms	11.29	11.00
t-C_5H_{11}	181	Needles or flattened prisms	10.69	10.75
cyc-C_6H_{11}	261–2[c]	Flattened prisms	10.21	10.11

[a] Beilstein, 4th ed., Vol. XIII, p. 133. [b] *Ibid.*, p. 177. [c] The diaminocyclohexylbenzene (presumably the 2,4-compound) recrystallized from water or heptane: m. p. 105–106°. Calcd.: N, 14.74. Found: N, 14.42.

NOTE 2.—In some cases the monoaminoalkylbenzene–tin chloride complex was quite insoluble in dilute acid solution and precipitated when the reduction solution was poured into water. In such cases, the precipitate could be differentiated from unreduced nitro compound by extracting with ether and testing with alkali.

Identification of *n*- and Isopropylbenzene in a Mixture with Each Other.—The diacetamino derivative of *n*-propylbenzene crystallizes from water or dilute alcohol in the form of soft, white, feathery aggregates (spherical clusters) which are seen to be made up of short thread-like crystals when viewed under high magnification. On filtering, the aggregates are easily broken up and a powdery material is obtained. The isomeric isopropyl derivative, on the other hand, crystallizes in the form of hard, glistening prisms which retain their shape even when filtered. These are anisotropic and show up beautifully in the polarizing microscope with crossed nicols, whereas under the same conditions the diacetamino-*n*-propylbenzene crystals are barely visible.

These rather surprisingly marked differences in the crystalline properties of the derivatives at once suggested a means for distinguishing each in a mixture of the two. Experiments which were made with synthetic mixtures gave very satisfactory results. The more vigorous nitrating mixture was used so as to lead eventually to the production of the diacetamino derivatives. The nitration and subsequent reduction proceeded smoothly. When acetic anhydride was added to the mixture of diamines, the acetamino derivatives crystallized out almost immediately. Water was added to hydrolyze the excess anhydride, and the mixture was heated until all of the derivative dissolved.

On cooling, there crystallized white feathery crystals, having the physical appearance of the diacetamino-*n*-propylbenzene. When viewed under the microscope, it was chiefly the short needles of the *n*-propylbenzene derivative which were seen. The melting point of the material so obtained was 202–204°, indicating the presence of a small amount of the isomeric compound. The mother liquor from this first crystallization, then, contained the major portion of the more soluble isopropylbenzene derivative. Hence, it was evaporated to about 3 cc. and allowed to stand. Crystals soon appeared and even with the unaided eye the glistening flakes of diacetaminoisopropylbenzene could be discerned. When examined under the microscope, both the small needles of the *n*-propylbenzene derivative and the large prisms of the isomeric isopropyl derivative were observed. When the nicols were crossed, the former disappeared from view and the latter shone brilliantly in the dark field.

After several fractional crystallizations from hot water the isopropyl derivative was isolated in an almost pure state, m. p. 214°.

Acknowledgment.—We wish to thank Dr. J. D. Kurbatov for assistance in the study of the crystal forms and Mr. R. W. Moehl for taking the photomicrograph.

Summary

A simple, uniform procedure is described for the preparation of the mono- and the diacetamino derivatives of monoalkylbenzenes. The physical properties of a series of such compounds is given.

Nitration of the alkylbenzene is shown to yield either the mononitro or the dinitro derivative or a mixture of both depending upon (a) the nature of the side chain, and (b) the composition of the nitrating mixture.

Under the prescribed conditions the *p*-acetaminoalkylbenzene was obtained unadmixed with ortho or meta isomers.

A method is presented for separating monoaminoalkylbenzenes from diaminoalkylbenzenes, based on the solubility in ether of the monoamine–tin chloride–hydrogen chloride complex.

It is shown that by means of the diacetamino derivatives it is possible to distinguish between the two propylbenzenes, when they occur either separately or in a mixture with each other.

RIVERSIDE, ILLINOIS RECEIVED APRIL 14, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in the Ketone Sugar Series. VII.
The Action of Titanium Tetrachloride on the Methylfructoside Acetates

BY EUGENE PACSU AND FRANCIS B. CRAMER

It has been shown in a series of investigations[1] that titanium tetrachloride is capable of transforming the acetylated β-alkyl glycosides and the fully acetylated derivatives of the aldoses into the corresponding α-forms. A characteristic of the reaction appears to be the formation of halochromic addition compounds which do not occur when stannic chloride[2] is employed to promote the same transformation. It has also been shown that the α-acetates of the sugars undergo a secondary change and are smoothly transformed to the corresponding α-acetochloro compounds. In order to test the generality of the conversion it seemed necessary to submit a ketose derivative, tetraacetyl-β-methylfructoside <2,6>, to the action of titanium tetrachloride. A yellow halochromic salt was produced immediately when this reagent was added to the chloroform solution of the fructoside. Contrary to expectation, no conversion into the α-form could be detected after the mixture had been heated for four hours. Neither did the starting material undergo any secondary reaction, since only unchanged tetraacetyl-β-methylfructoside was recovered after the reaction mixture had been worked up in the usual way. Such behavior of the β-methylfructoside acetate might be compared with that of β-pentaacetylfructose <2,6> which has been shown in Part VI[3] to undergo isomerization into the α-form only to a very slight extent when treated with zinc chloride in acetic anhydride solution. Since α-pentaacetylfructose <2,6>, on the other hand, has been found to suffer a rapid and almost complete conversion into the β-pentaacetate of fructose in the presence of zinc chloride, it was thought that tetraacetyl-α-methylfructoside <2,6> might readily rearrange into the β-isomer when treated with titanium tetrachloride. The result of the experiment was an unexpected one. The reaction product

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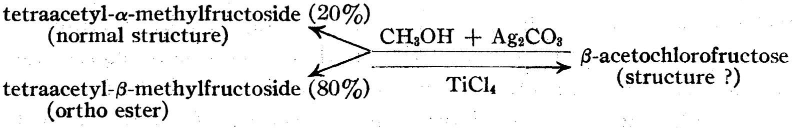
[1] Pacsu, *Ber.*, **61**, 1508 (1928); THIS JOURNAL, **52**, 2563, 2568, 2571 (1930).

[2] Pacsu, *Ber.*, **61**, 137 (1928).

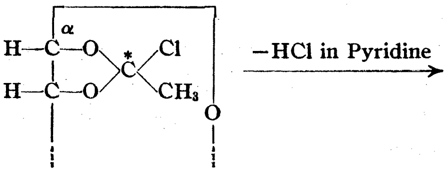
[3] Cramer and Pacsu, THIS JOURNAL, **59**, 711 (1937).

was found to be β-acetochlorofructose, with which unchanged starting material was admixed. The presence of unchanged α-fructoside in connection with the result of the previous experiment shows that no conversion into the β-fructoside could have taken place. It is to be concluded, therefore, that titanium tetrachloride is without any action on the methylglycosidic group of fructose of β-configuration, but that it easily replaces the glycosidic group of fructose of α-configuration with a chlorine atom. At present, any interpretation of this strange behavior is conjectural.

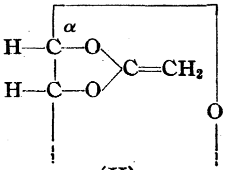
Tetraacetyl-α-methylfructoside <2,6> has recently been shown[4] to be the true diastereomer of tetraacetyl-β-methylfructoside which, according to Haworth,[5] possesses a normal structure. On the strength of the above experiment, one may infer that the formation of β-acetochlorofructose from the α-fructoside proves definitely that β-acetochlorofructose itself possesses normal structure as is generally assumed although not proved by direct evidence. On the other hand, the formation of about 80% of the tetraacetylmethylfructoside having ortho ester structure from β-acetochlorofructose, which reaction has recently been shown[6] to take place when using standard procedures, might be construed as evidence that β-acetochlorofructose has an ortho ester structure. Therefore, a study of the action of titanium tetrachloride on the tetraacetylmethylfructoside with ortho ester structure was made. Formation of a new acetochlorofructose would have established beyond doubt the structure and would have confirmed indirectly the normal structure of β-acetochlorofructose. However, it was found that the reaction yielded pure β-acetochlorofructose as the only crystalline product. Similarly, rapid formation of β-acetobromofructose was observed when this methylfructoside acetate was treated with hydrogen bromide dissolved in glacial acetic acid. In the light of these transformations β-acetochlorofructose appears to be a substance which readily undergoes molecular rearrangement. Obviously, it is not possible to prove by the above chemical methods whether β-acetochlorofructose possesses a normal or an ortho ester structure.



The only authentic representative of an acetohalogenose with ortho ester structure appears to be Freudenberg's "third acetochloromaltose"[7] (I). The allocation of an ortho ester structure[8] to this compound is justified not so much by its giving rise to an ortho ester α-methylmaltoside acetate as by the fact that it represents a surplus isomer which demands a chemical formula that is in harmony with the present views on the structure of maltose. The difference in the behavior of a freshly prepared and a several days old pyridine solution of this unstable "third acetochloromaltose" toward potassium permanganate was suggested by Freudenberg as being due to the formation of a ketene acetal (II).



(I)



(II)

In Part VI[3] it has been shown that crystalline acetochloro- and acetobromoturanose, which were previously described[9] as possessing ortho ester structures, exhibit common properties with acetochloro- and acetobromofructose. In aged pyridine solution the bromo derivatives develop reducing power toward potassium permanganate, whereas the more stable acetochloro compounds do not and can be recovered unchanged. The ability of several days old pyridine solutions of certain acetohalogenoses to reduce potassium permanganate might be due to slight decomposition, since some coloration always occurs during that period of time. Therefore, unless ketene acetals are actually *isolated*, their assumed formation in pyridine solutions cannot be used as evidence for the ortho ester structures of the aceto

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[4] Pacsu and Cramer, THIS JOURNAL, **57**, 1944 (1935).

[5] Haworth, Hirst and Learner, *J. Chem. Soc.*, 1040 (1927).

[6] Pacsu, THIS JOURNAL, **57**, 745 (1935).

[7] Freudenberg and Ivers, *Ber.*, **55**, 929 (1922); Freudenberg, Hochstetter, and Engels, *ibid.*, **58**, 666 (1925).

[8] Freudenberg, *Naturwissenschaften*, 393 (1930); Freudenberg and Scholz, *Ber.*, **63**, 1969 (1930).

[9] Pacsu, THIS JOURNAL, **54**, 3649 (1932).

halogenoses. Notwithstanding this conclusion, Freudenberg's acetochloromaltose may very well possess ortho ester structure which, although unproved by chemical evidence, is suitable as an explanation for the existence of this surplus isomer. The existence of this compound makes it possible to determine whether a methylglycoside acetate with ortho ester structure, on treatment with titanium tetrachloride or hydrogen bromide, will give back a halogeno compound of the same "abnormal" structure, or will suffer rearrangement and give rise to the "normal" acetohalogenose. Accordingly, a chloroform solution of α-methylmaltoside acetate with ortho ester structure was treated with titanium tetrachloride. The product of the reaction was found to be the normal α-acetochloromaltose. In another experiment, when dry hydrogen bromide dissolved in glacial acetic acid was used, a rapid formation of the normal α-acetobromomaltose was observed. Obviously, in the following transformations

$$\underset{\text{(ortho ester)}}{\alpha\text{-acetochloromaltose}} \xrightarrow{CH_3OH + Ag_2CO_3} \underset{\text{(ortho ester)}}{\alpha\text{-methylmaltoside acetate}} \xrightarrow{TiCl_4} \underset{\text{(normal)}}{\alpha\text{-acetochloromaltose}} \xrightarrow{CH_3OH + Ag_2CO_3} \underset{\text{(normal)}}{\beta\text{-methylmaltoside acetate}}$$

the replacement of the methoxyl group of the ortho ester glycoside by a halogen atom is accompanied by a rearrangement of the ortho ester molecule. A similar case, where titanium tetrachloride had been used on an ortho ester glycoside of an aldose, was recorded by Isbell.[10] He found that, when treated with titanium tetrachloride, the heptaacetyl-4-glucosido-"γ"-methylmannoside gave back the known chloroheptaacetyl-4-glucosidomannose which is considered to be of normal structure.

If the very plausible assumption is made that not only the ortho ester methylmaltoside acetate, but *any* ortho ester glycoside will suffer rearrangement when treated with titanium tetrachloride into what is regarded as the normal acetohalogenose, then this reaction can be used to ascertain the structure of those acetohalogenoses from which the ortho ester glycosides have been prepared. On this basis, the crystalline acetohalogenoses of fructose and turanose now appear to possess normal structures. The acetohalogeno derivatives of turanose were previously described[9] as ortho esters. This was done partly because the two octaacetates from which they had been prepared were considered as ortho ester derivatives. However, in Part VI[3] it has been pointed out that, at present, it is not possible to determine whether any sugar acetate possesses normal or ortho ester structure. Therefore, only the surplus *number* of turanose octaacetates, now five altogether, demand that other than normal structures should be assigned some of them in order to avoid conflict with the accepted structure of turanose. This sugar, being regarded as 6-glucosidofructose[11] or 5-glucosidofructose,[12,13] permits the existence of only three acetates excluding ortho esters, namely, the open-chain acetate and an α,β-pair of octaacetates. On this basis, unless the unwarranted assumption is made that some of the five acetates possess ring structures other than pyranoid or furanoid, the number of isomers demands that both the fifth and sixth carbon atoms in the fructose constituent must carry unoccupied hydroxyl groups. In this difficult situation a complete reinvestigation of the structure of turanose becomes necessary. The structure of this disaccharide was based on methylation experiments that gave a sirupy trimethylfructose. Using the method of elimination, Zemplén[11,12] concluded that his product contained the methyl groups in the 1,3,4-positions. This was later confirmed by Leitch.[14] Crystalline 1,3,4-trimethylfructose with m. p. 75° subsequently was described by several investigators.[15] Since Zemplén's sirupy product shows $[\alpha]_D + 30°$ in water and $+25°$ in alcohol solution, and Leitch's product has the rotation $+55.5°$ in alcohol solution, it appears that the identity of this key substance with the crystalline 1,3,4-trimethylfructose having $[\alpha]^{18}_{5780}$ $-52°$ in water solution is questionable.

Experimental Part

Treatment of β-Methylfructoside Tetraacetate with Titanium Tetrachloride.—To 2.0 g. of β-methylfructoside tetraacetate (specific rotation[16] −124°) dissolved in 200 cc. of absolute chloroform was added 3.7 g. (3.5 mols) of titanium tetrachloride in 25 cc. of the same solvent. An insoluble yellow halochromic salt formed. After heating

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(10) Isbell, *Bur. Standards J. Research*, **7**, 1120 (1931).

(11) Zemplén, *Ber.*, **59**, 2539 (1926).

(12) Zemplén and Braun, *ibid.*, **59**, 2230 (1926).

(13) Pacsu, THIS JOURNAL, **53**, 3099 (1931).

(14) Leitch, *J. Chem. Soc.*, 588 (1927).

(15) Hibbert and Tipson, THIS JOURNAL, **52**, 2582 (1930); Challinor, Haworth and Hirst, *J. Chem. Soc.*, 676 (1934).

(16) Unless otherwise stated, all specific rotations recorded in this paper were observed at 20° C. using light of the wave length of the sodium D lines with chloroform as solvent.

it at 55–60° for four hours, the mixture was worked up in the usual way.[1] The sirupy product had the specific rotation −117°. This was again dissolved in absolute chloroform and refluxed for one hour with 2.1 g. (2 mols) of titanium tetrachloride. Upon working up the mixture as before, a sirup was obtained having the unchanged rotation −117°. The material contained no chlorine and did not reduce Fehling's solution. In an acetyl estimation, 0.1686 g. of sirup required 17.1 cc. of 0.1 *N* sodium hydroxide solution. The calculated value for four acetyls is 18.6 cc.

Action of Titanium Tetrachloride on α-Methylfructoside Tetraacetate.—To 2.0 g. of α-methylfructoside tetraacetate (specific rotation 45.5°) dissolved in 185 cc. of absolute chloroform was added 3.7 (3.5 mols) of titanium tetrachloride in 15 cc. of the same solvent. The mixture was heated at 55–60° for three and one-half hours and refluxed for one hour. Upon working up the material, a sirup was obtained having the specific rotation −63° and giving a strong test for labile halogen. The sirup was dissolved in 200 cc. of absolute chlorofrom and refluxed with 2 g. (2 mols) of titanium tetrachloride for one hour. Considerable material was lost due to emulsification while working up the reaction mixture. The 0.9 g. of sirup obtained had the specific rotation −70.4°. The ether solution of the substance deposited in several crops 0.44 g. of a crystalline mixture from which 0.09 g. of α-methylfructoside tetraacetate and 0.07 g. of β-acetochlorofructose were isolated in pure condition and identified by their specific rotations and melting points.

Action of Titanium Tetrachloride on Ortho Ester Methylfructoside Tetraacetate.—The material used in this experiment was prepared by the first method described in Part IV,[6] was without action on Fehling's solution, contained about 6% of α-methylfructoside tetraacetate, and had the specific rotation −8.6°. To 4.0 g. of this substance dissolved in 100 cc. of absolute chloroform was added 2.1 g. (1 mol) of titanium tetrachloride in 25 cc. of the same solvent. An insoluble yellow halochromic salt formed. After refluxing for one hour the mixture had become brown and was worked up immediately. The ether solution of the product deposited 1.2 g. of crystalline material which, after recrystallization, had the correct specific rotation and melting point of β-acetochlorofructose.

Formation of β-Acetobromofructose from Ortho Ester Methylfructoside Tetraacetate and Hydrogen Bromide.—To 0.6859 g. of ortho ester methylfructoside tetraacetate dissolved in 10 cc. of absolute chloroform was added 6 cc. of glacial acetic acid saturated with hydrogen bromide at 0°, the solution was made up to 25 cc. with chloroform and, after mixing, was poured into a polarimeter tube. In five minutes the specific rotation had become −187°, and after ten minutes it remained constant at −194°. The specific rotation of β-acetobromofructose in pure chloroform is −189.1°.

Action of Titanium Tetrachloride on Ortho Ester Methylmaltoside Heptaacetate.—To 0.7 g. of ortho ester methylmaltoside heptaacetate dissolved in 40 cc. of absolute chloroform was added 0.3 g. (1.4 mol) of titanium tetrachloride in 10 cc. of the same solvent. An insoluble yellow halochromic salt formed. After refluxing for one hour, the mixture was worked up. The solid product obtained had the specific rotation 144°. Pure α-acetochloromaltose crystallizes with difficulty and has the specific rotation 159.5°. The "third acetochloromaltose" of Freudenberg has the specific rotation 67.5°.

Formation of α-Acetobromomaltose from Ortho Ester Methylmaltoside Heptaacetate and Hydrogen Bromide.—To 0.0976 g. of ortho ester methylmaltoside heptaacetate dissolved in 6 cc. of absolute chloroform was added 1 cc. of glacial acetic acid saturated with hydrogen bromide at 0°. The solution was made up to 10 cc. with chloroform and transferred to a polarimeter tube. The specific rotation increased rapidly until after one and one-half hours it remained constant at 188°. The specific rotation of α-acetobromomaltose in pure chloroform is 180.1°.

Summary

1. Unlike the β-alkylglycoside acetates of the aldoses, tetraacetyl-β-methylfructoside <2,6>, on treatment with titanium tetrachloride, does not suffer rearrangement into the α-form. Neither does it undergo any secondary reaction, since only unchanged starting material can be recovered. Similarly treated tetraacetyl-α-methylfructoside <2,6> gives rise to the known β-acetochlorofructose, but no conversion into the β-glycoside takes place. Also, tetraacetylmethylfructoside with ortho ester structure yields pure β-acetochlorofructose and not a new acetochlorofructose with ortho ester structure as might be expected.

2. Methylmaltoside heptaacetate with ortho ester structure, on treatment with titanium tetrachloride, gives rise to normal α-acetochloromaltose and not to the "third acetochloromaltose" from which it has been prepared. In the light of this reaction, the acetohalogeno derivatives of fructose and turanose appear to have normal structures.

3. The existence of five octaacetates of turanose in connection with certain other facts makes a reinvestigation of the structure of turanose necessary.

PRINCETON, NEW JERSEY RECEIVED MARCH 13, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Mechanism of Substitution Reactions: the Reaction of Benzyl Chloride with Mercuric Salts[1]

BY IRVING ROBERTS AND LOUIS P. HAMMETT

By far the most illuminating picture of the typical substitution reaction of organic chemistry is that suggested by London[2] and developed and applied by Polanyi[3] and by Olson.[4] In this there is a simultaneous addition and dissociation of reactants, a simultaneous formation and breaking of linkages. Thus in the reaction of an alkyl chloride with iodide ion[5]

$$I^- + R_3CCl \longrightarrow ICR_3 + Cl^- \quad (1)$$

the carbon–iodine linkage is thought of as being formed at the same time that the carbon–chlorine linkage is dissociating. While the stereochemical corollaries of this mechanism are important and have been considerably investigated[3b,4b] the energetics of the process lead to even more interesting conclusions. It is in fact an essential part of this theory that the energy of formation of a new linkage may contribute largely toward doing the very considerable amount of work necessary to break an old one. In the above example it is possible to break the carbon–chlorine linkage only because the simultaneous formation of the carbon–iodine linkage involves a considerable decrease in potential energy. In terms of this energy interchange or compensation we can immediately understand the principle which every organic chemist uses that silver salts are the proper reagents to react with chlorine compounds and that strong acids like sulfuric are the proper reagents to use in condensation reactions of hydroxyl compounds. The reason is that the large energy of formation of silver halide or of water furnishes the necessary driving force. Reactions of the type of equation (1) have been much investigated as have also the undoubtedly similar reactions of the type[6]

$$H_3N + R_3CCl \longrightarrow H_3NCR_3^+ + Cl^- \quad (2)$$

There is, however, an entirely different class of reactions of alkyl halides in which the driving force is clearly derived from the energy of formation of a linkage of halide ion to metallic ion. For instance, the rate of hydrolysis of an alkyl halide may be increased by several orders of magnitude by the addition of silver or mercuric salts. This important type of reaction has been subjected to detailed kinetic study in only one case, the reaction of silver nitrate with alkyl halides. Unfortunately, this particular reaction is badly complicated by a pronounced catalysis by the solid silver halide formed in the reaction.[7]

We have therefore studied the corresponding mercuric nitrate reaction with benzyl chloride for which this complication does not exist. As in the silver nitrate reaction, benzyl nitrate is formed in addition to the benzyl alcohol which results from the hydrolysis. The stoichiometric equations are

$$2C_6H_5CH_2Cl + Hg(NO_3)_2 \longrightarrow 2C_6H_5CH_2NO_3 + HgCl_2 \quad (3)$$

$$2C_6H_5CH_2Cl + Hg(NO_3)_2 + 2H_2O \longrightarrow 2C_6H_5CH_2OH + 2HNO_3 + HgCl_2 \quad (4)$$

The total rate of reaction of mercuric nitrate and benzyl chloride could therefore be followed by titration of the mercuric nitrate with chloride ion using diphenylcarbazide indicator,[8] while the relative amounts of the two products benzyl nitrate and benzyl alcohol could be determined by an acidimetric titration. As media we have used dioxane–water mixtures containing 60, 75 and 95% dioxane by volume. These were used because the resulting reaction mixtures are homogeneous, and because the solvent does not react with mercuric compounds, as do alcoholic and ketonic solvents.

The Kinetic Order of the Reaction

The reaction is essentially a second order one of mercuric nitrate and benzyl chloride, uncomplicated by reversibility, or by hydrolysis of benzyl nitrate. There are, however, appreciable de-

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[1] Dissertation submitted by Irving Roberts in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. The material was presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.

[2] London, *Z. Elektrochem.*, **35**, 552 (1929).

[3] (a) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); (b) Bergmann, Polanyi and Szabo, *ibid.*, **B20**, 161 (1933).

[4] (a) Olson, *J. Chem. Phys.*, **1**, 418 (1933); (b) Olson and Voge, THIS JOURNAL, **56**, 1690 (1934).

[5] Conant and Kirner, *ibid.*, **46**, 232 (1924); Conant and Hussey, *ibid.*, **47**, 476 (1925).

[6] Menschutkin, *Z. physik. Chem.*, **17**, 193 (1895); Hammett and Pfluger, THIS JOURNAL, **55**, 4079 (1933).

[7] Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1904); Burke and Donnan, *Z. physik. Chem.*, **69**, 148 (1909); Donnan and Potts, *J. Chem. Soc.*, **97**, 1882 (1910); Senter, *ibid.*, **97**, 357 (1910); Baker, *ibid.*, 990 (1934).

[8] Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).

viations from second order kinetics which are very important for the understanding of the nature of the reaction. A systematic study of the initial rate of reaction showed that it is rigidly first order with respect to benzyl chloride and unaffected by the addition of benzyl nitrate or of benzyl alcohol under all conditions studied. In 75% dioxane, but not in the other media, the reaction is essentially first order with respect to mercuric nitrate, and the rate is unaffected by the addition of mercuric chloride and only slightly affected by the addition of inorganic nitrates. Nevertheless, the second order constant obtained in this medium showed a steady downward drift during the course of the reaction.

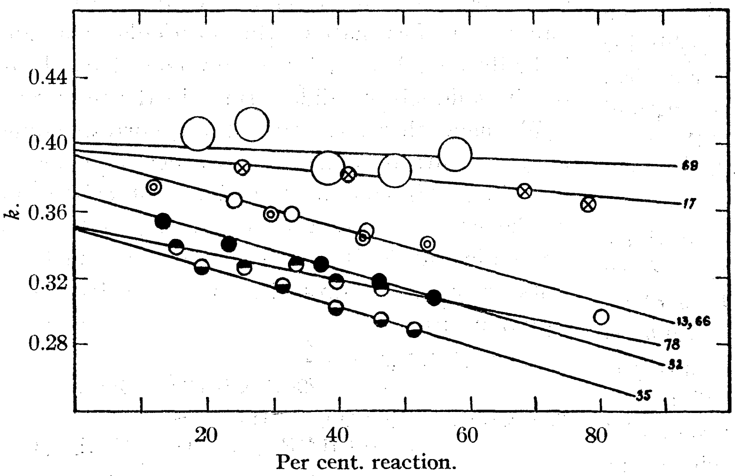

Fig. 1.—The retarding effect in 75% dioxane: ◉ no. 66, $(Hg(NO_3)_2) = 0.025$ *N*, $(BCl) = 0.050$ *N*; ○ no. 13, $(Hg(NO_3)_2) = 0.025$ *N*, $(BCl) = 0.025$ *N*; ⊗ no. 17, $(Hg(NO_3)_2) = 0.050$ *N*, $(BCl) = 0.025$ *N*; ○ no. 69, $(Hg(NO_3)_2) = 0.105$ *N*, $(BCl) = 0.025$ *N*; ● no. 32, a reaction in which $(Hg(NO_3)_2) = (BCl) = 0.025$ *N* is allowed to go to completion, new reactants (0.025 *N*) were then added and the kinetics followed; ◒ no. 35, a reaction in which $(Hg(NO_3)_2) = (BCl) = 0.050$ *N* is allowed to go to completion, new reactants (0.025 *N*) were then added and the kinetics followed; ◓ no. 78, 0.025 *N* $HgCl_2$, $Hg(NO_3)_2$, and BOH allowed to stand for seven hours, BCl was then added and the kinetics followed.

The Retarding Secondary Reaction.—In Fig. 1 we have plotted the second order rate constant *k* against the per cent. of reaction for a number of initial conditions, the solvent being in every case 75% dioxane. The radius of each circle represents the probable error. This is especially large in expt. 69 because of the exceptionally high rate. The resulting series of points, for a given experiment, is linear within experimental error and can be extrapolated satisfactorily to give the initial constant. The identity of the values of this initial constant for expts. 13, 66, 17 and 69, which involve different concentrations of mercuric nitrate and benzyl chloride, demonstrates the true second order nature of the initial reaction. The decrease in slope observed as the concentration of mercuric nitrate is increased suggests that a retarding factor operates by preventing some of the mercuric nitrate from participating in the reaction. Although none of the previously known products of the reaction retard it, something produced in the reaction does retard, as the data plotted in lines 32 and 35 of Fig. 1 demonstrate. Here new mercuric nitrate and benzyl chloride were added to spent reaction mixtures and the extrapolated initial reaction rates were found to be considerably decreased. The magnitude of this decrease was 6.5% when the initial mixture contained 0.025 *N* concentrations of mercuric nitrate and benzyl chloride (expt. 32); it was 11.5% when these concentrations were 0.05 *N* (expt. 35).

To isolate this retarding substance, a large amount of reaction mixture of high concentration (1.0 *N*) was prepared, and the reaction product was subjected to various operations of separation. The efficacy of each such operation was tested by observing the effect of the fractions upon the rate of the mercuric nitrate–benzyl chloride reaction. In this way a new substance which possesses a marked retarding effect upon the reaction was isolated. This substance has the composition of a chloromercuri-benzyl alcohol, and the properties of a weak acid. Its structure has not yet been determined. Subsequently it was found that this substance can be prepared by the action of mercuric nitrate upon benzyl alcohol followed by the addition of chloride ion, and it is apparently produced during the mercuric nitrate–benzyl chloride reaction in this way, the benzyl alcohol being produced in the primary reaction.

That this compound is at least partly responsible for the deviation from the second order course of the primary reaction is shown by the data of line 78 of Fig. 1. Here the new compound was allowed to form by the reaction of mercuric nitrate, mercuric chloride and benzyl alcohol. When benzyl chloride was added the initial reaction rate was as low as in expt. 35. It should be noted that separate experiments showed that the mere presence without previous reaction of benzyl alcohol and mercuric chloride in a reaction mixture has a negligible effect upon the rate.

That there are still further complications due to side reactions is demonstrated by the fact that the slope of 32, 35 and 78 is no greater than that of lines 13 and 66, whereas the initial presence of benzyl alcohol in these runs would be expected to produce a more rapid formation of the retardant and greater drift in the second order constants. It seems evident, however, that no matter how involved the mechanism of the drift, its cause is a subsequent reaction of a product of the primary reaction. Consequently, we can assume that the initial extrapolated second order constant is the correct one for the mercuric nitrate–benzyl chloride reaction. That this secondary reaction also takes place in 60% dioxane even though the constant increases during the course of the reaction, is evidenced by the fact that the same retardant compound can be isolated from this medium in about the same yield as from 75% dioxane.

The Effects of Nitrates and of Perchlorates.—Nitrates accelerate the reaction in all the media studied, but the effect is largest in 60% dioxane, in which there also appears a deviation from proportionality between rate and mercuric nitrate concentration. The effect of added nitrates in the 60% mixture is shown in Table I and plotted in Fig. 2. The three nitrates used have practically the same effect at equivalent concentrations. Some measurements with calcium nitrate deviate considerably but have been omitted because the solutions were turbid, showing that some complication enters in this case. As Table II shows, a decrease in mercuric nitrate concentration with a constant concentration of nitric acid produces an increase in the second order constant.

TABLE I

EFFECT OF NITRATES AND PERCHLORATES ON k IN 60% DIOXANE. $(BCl)^a = 0.025$ N

Expt.	Reactant	Other electrolytes	k
45	0.025 N $Hg(NO_3)_2$	0.013 N HNO_3	0.956
53	.025 N $Hg(NO_3)_2$	.030 N HNO_3	1.002
54	.025 N $Hg(NO_3)_2$	.085 N HNO_3	1.070
61	.025 N $Hg(NO_3)_2$	.140 N HNO_3	1.080
59	.025 N $Hg(NO_3)_2$	.013 N HNO_3 .06 N KNO_3	1.042
60	.025 N $Hg(NO_3)_2$	.013 N HNO_3 .15 N KNO_3	1.060
62	.025 N $Hg(NO_3)_2$	.013 N HNO_3 .135 N $Mg(NO_3)_2$	1.078
51	.025 N $Hg(ClO_4)_2$	.016 N $HClO_4$	1.320
52	.025 N $Hg(ClO_4)_2$	.037 N $HClO_4$	1.406
63	.025 N $Hg(NO_3)_2$	.013 N HNO_3 .045 N $KClO_4$	1.122

[a] B = benzyl, $C_6H_5CH_2$.

TABLE II

EFFECT OF $(Hg(NO_3)_2)$ ON k IN 60% DIOXANE $(BCl) = 0.025$ N

Expt.	$Hg(NO_3)_2$, N	HNO_3, N	k
65	0.050	0.029	0.956
53	.025	.030	1.002
74	.012	.030	1.038

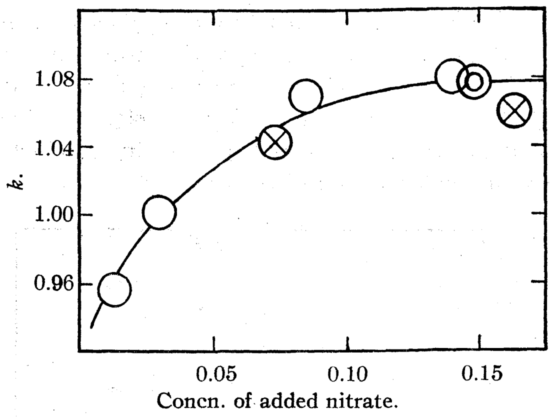

Fig. 2.—Effect of added nitrate on k in 60% dioxane: ○, HNO_3; ⊗, KNO_3; ◉, $Mg(NO_3)_2$.

These phenomena are no doubt due in part to salt effects, and it is therefore impossible to decide from them alone whether the actual reactant is mercuric ion, non-ionized mercuric nitrate, or the intermediate ion $HgNO_3^+$. Conclusive evidence that mercuric ion is not the sole reactant is, however, offered by our experiments with mercuric perchlorate. This reacts much more rapidly with benzyl chloride than does the nitrate, as experiments 51 and 52 in Table I demonstrate. Furthermore, the addition of alkali perchlorate to mercuric nitrate results in a considerably increased rate (expt. 63). Consequently some new more reactive substance is formed when perchlorate is added to the nitrate solution and this can only be $Hg(ClO_4)_2$ or $HgClO_4^+$. But there may be expected to be even more non-ionized nitrate in the mercuric nitrate solution than there is non-ionized perchlorate in the mercuric perchlorate solution, because of the considerably greater tendency toward the formation of non-ionogen compounds exhibited by nitrate ion. The idea that these mercuric salts should not be completely ionized is entirely reasonable in view of the known tendency of mercuric salts toward complex formation and the favorable effect of the low dielectric constant of the medium.

The Effect of Mercuric Chloride.—As has been stated previously, addition of mercuric chloride to the reaction mixture in 75% dioxane has no effect upon the rate. In 95% dioxane, however, 0.05 *N* mercuric chloride lowers the rate constant from 0.116 to 0.072. Since mercuric chloride is produced as the reaction goes on, this negative catalysis explains the larger downward drift found in this medium, a drift so large as to make accurate extrapolation difficult. On the other hand, in 60% dioxane where mercuric chloride speeds up the reaction, the small upward drifts or constant values of the specific rate observed may be attributed to the opposing effects of the retarding secondary reaction and the accelerating products, mercuric chloride and nitric acid.

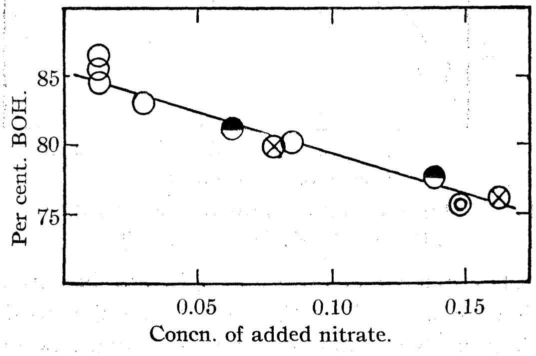

Fig. 3.—Effect of added nitrate on % BOH in 60% dioxane: ○, HNO_3; ⊗, KNO_3; ◎, $Mg(NO_3)_2$; ◓, $Ca(NO_3)_2$.

Table III shows the effect of mercuric chloride on the velocity in 60% dioxane. Concentrations higher than 0.04 *N* could not be used because of the low solubility of mercuric chloride in this medium. It can be seen, however, that the catalysis is a large one with no sign of levelling off in this concentration range.

TABLE III

EFFECT OF MERCURIC CHLORIDE ON *k* IN 60% DIOXANE

(BCl) = 0.025 *N*

Expt.	Reactant	Acid	$HgCl_2$, *N*	*k*
45	0.025 *N* $Hg(NO_3)_2$	0.013 *N* HNO_3	0.000	0.956
49	.025 *N* $Hg(NO_3)_2$	.013 *N* HNO_3	.026	1.130
50	.025 *N* $Hg(NO_3)_2$	.013 *N* HNO_3	.039	1.184
64	.025 *N* $Hg(ClO_4)_2$	016 *N* $HClO_4$	.040	1.924

Morse[9] has demonstrated the existence in water of the ion $HgCl^+$ as the result of the first dissociation of mercuric chloride. The equilibrium constant for the equilibrium $HgCl_2 + Hg^{++} \rightleftarrows 2HgCl^+$, is the quotient of the first and second dissociation constants of mercuric chloride and has a value of about 8 in water. The above data on the effect of mercuric chloride on the reaction are completely explained if we assume that $HgCl^+$ (or $HgClNO_3$ in this solvent) also reacts with benzyl chloride. The differing effects of mercuric chloride in the various media may be attributed to a shift in the above equilibrium and in the relative velocities of the $Hg(NO_3)_2$ and the $HgClNO_3$ reactions.

The Distribution of Products

The most striking property of the reaction of silver nitrate with alkyl halides is the complete lack of dependence of the proportion of alkyl nitrate in the reaction product upon the concentration of ionic nitrate in the reacting mixture. By contrast, the mercuric nitrate reaction shows a distribution of product between benzyl alcohol and benzyl nitrate which varies with varying concentration of nitric acid or alkali nitrate in the solution. The results in 60% dioxane are shown in Table IV and plotted in Fig. 3. The distribution is, however, effectively independent of the concentration of mercuric nitrate as Table V indicates. This result supports our previous conclusion that much of the mercuric nitrate is in the non-ionized condition.

TABLE IV

EFFECT OF ADDED NO_3^- ON % BOH IN 60% DIOXANE

($Hg(NO_3)_2$) = (BCl) = 0.025 *N*

	Added NO_3^-	%BOH
HNO_3	0.013 *N*	86.5, 84.5, 85.5
HNO_3	.030	83.0
$Ca(NO_3)_2$	.063	81.1
KNO_3	.073	79.9
HNO_3	.085	80.2
$Ca(NO_3)_2$	.138	77.7
$Mg(NO_3)_2$	.148	75.7
KNO_3	.163	76.1

TABLE V

EFFECT OF ($Hg(NO_3)_2$) ON % BOH IN 60% DIOXANE

(BCl) = 0.025 *N*

$Hg(NO_3)_2$, *N*	HNO_3, *N*	%BOH
0.050	0.029	81.3
.025	.030	83.0
.012	.030	82.2

Table VI shows that mercuric chloride has no effect on the distribution of products, although it has a large effect on the velocity of the reaction (Table III).

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(9) Morse, *Z. physik. Chem.*, **41**, 709 (1902).

TABLE VI

EFFECT OF ($HgCl_2$) ON % BOH IN 60% DIOXANE

($Hg(NO_3)_2$) = (BCl) = 0.025 *N*; (HNO_3) = 0.013 *N*

$HgCl_2$, *N*	% BOH
0.000	85.5 (mean of 3)
.026	86.5
.039	85.4

The effect of nitrates and the lack of effect of mercuric chloride on the distribution applies in the same way to 75% dioxane. The percentage of benzyl alcohol decreases as the amount of dioxane in the medium is increased: in 75% dioxane, 68% of the product is benzyl alcohol, and in 95% dioxane, 35% of the product is benzyl alcohol.

In the perchlorate experiments in 60% dioxane the product is 100% benzyl alcohol during the whole course of the reaction, even in the presence of excess perchlorate. In the mixed nitrate–perchlorate run (expt. 63, Table I) the product was found to be 88.6% benzyl alcohol, an intermediate value.

The Mechanism of the Reaction

The possibilities may be classified into three general types.

(1) **Double Decomposition,** AB + CD ⟶ AC + BD.—Let us consider a pair of concurrent reactions, one of mercuric nitrate or of $HgNO_3^+$ to form benzyl nitrate, and one of mercuric ion, which is of course hydrated, to form benzyl alcohol. If we use the most probable formulas with a coördination number of four for the mercuric ion, the equations are

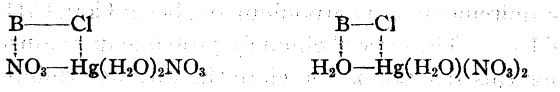
$$C_6H_5CH_2Cl + Hg(H_2O)_2(NO_3)_2 \longrightarrow C_6H_5CH_2NO_3 + Hg(H_2O)_2NO_3Cl \quad (5)$$

$$C_6H_5CH_2Cl + Hg(H_2O)_4^{++} \longrightarrow C_6H_5CH_2OH + Hg(H_2O)_3Cl^+ + H^+ \quad (6)$$

As we have indicated previously, however, one of the actual reactants, when perchlorates are present, must be mercuric perchlorate or the ion $HgClO_4^+$. On the basis of this mechanism these reactants could only form benzyl perchlorate. Actually no measurable amount of perchlorate ester is formed at any time, and it is most improbable that it is formed as an unstable intermediate, because the known alkyl perchlorates are far from instantaneously hydrolyzed.[10] Therefore, since benzyl alcohol may be formed by the reaction of mercuric perchlorate, there is every reason to expect that it should be formed by the reaction of mercuric nitrate. We must therefore add a third equation to the first two

$$C_6H_5CH_2Cl + Hg(H_2O)_2(NO_3)_2 \longrightarrow C_6H_5CH_2OH + Hg(H_2O)(NO_3)_2Cl^- + H^+ \quad (7)$$

This reaction scheme would suppose two possible modes of addition of the hydrated mercuric nitrate to benzyl chloride, one leading to benzyl nitrate, the other to benzyl alcohol



$$\begin{array}{ccc} B\text{——}Cl & \qquad & B\text{—}Cl \\ \vdots \quad \vdots & & \vdots \quad \vdots \\ NO_3\text{—}Hg(H_2O)_2NO_3 & & H_2O\text{—}Hg(H_2O)(NO_3)_2 \end{array}$$

On this basis the greater rate of benzyl alcohol formation from mercuric perchlorate than from mercuric nitrate may be attributed to a weaker binding of the water molecules in hydrated mercuric perchlorate than in the nitrate.

The objections to this mechanism are two-fold. In the first place, if this one-step picture is correct, there should be a parallelism between the effect of nitrates on the reaction velocity and on the proportion of benzyl nitrate produced. Actually the curve showing the former levels off at about 0.1 *N* added nitrate (Fig. 2), while the latter shows a linear relationship with concentration (Fig. 3).

In the second place, the failure of mercuric chloride to affect the distribution requires, if this mechanism is adopted, the assumption that the ratio of the rates of formation of benzyl nitrate and of benzyl alcohol from $HgClNO_3$ be the same as the corresponding ratio for the formation from $Hg(NO_3)_2$. There is no reason to expect so simple a relationship, and still less to expect that it should occur in both 60 and 75% dioxane.

(2) **The Termolecular Mechanism** A + BC + D ⟶ AC + BD.—This would be formulated as follows

$$C_6H_5CH_2Cl + Hg^{++} + NO_3^- \longrightarrow C_6H_5CH_2NO_3 + HgCl^+ \quad (8)$$

$$C_6H_5CH_2Cl + Hg^{++} + H_2O \longrightarrow C_6H_5CH_2OH + H^+ + HgCl^+ \quad (9)$$

The objections are of the same nature as for the first case, from which this mechanism is indeed kinetically indistinguishable.

(3) **The Ionic Intermediate Mechanism.**—These difficulties vanish if it is supposed that the reaction proceeds through an unstable intermediate which can react either with nitrate ion to form benzyl nitrate or with water to form benzyl alcohol. The effects of added nitrates upon the total rate of reaction are exerted only upon the rate of

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[10] Ethyl perchlorate may be distilled from water without hydrolysis [Roscoe, *Ann.*, **124**, 124 (1862)]. The compound $Cl{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}ClO_4$ in 0.5 molar concentration is half hydrolyzed at 17° after forty hours [Hoffman, Zedwitz and Wagner, *Ber.*, **42**, 4390 (1909)].

formation of this intermediate, whereas the effect of nitrate upon the distribution depends upon an increased rate of formation of benzyl nitrate from the intermediate and nitrate ion. The two effects are consequently independent. Since mercuric chloride does not affect the distribution, the intermediate formed when the reactant is $HgClNO_3$ must be the same as when the reactant is $Hg(NO_3)_2$, and the only substance which fits these requirements is a carbonium ion, benzyl ion, $C_6H_5CH_2^+$. The overwhelmingly probable mechanism for this reaction is therefore the rate determining step

$$\left\{\begin{matrix} Hg(NO_3)_2(H_2O)_2 \\ HgClNO_3(H_2O)_2 \\ Hg(H_2O)_4^{++} \end{matrix}\right\} + C_6H_5CH_2Cl \longrightarrow \left\{\begin{matrix} HgClNO_3(H_2O)_2 + NO_3^- \\ HgCl_2(H_2O)_2 + NO_3^- \\ HgCl(H_2O)_3^+ + H_2O \end{matrix}\right\} + C_6H_5CH_2^+ \quad (10)$$

followed by the concurrent reactions

$$C_6H_5CH_2^+ + NO_3^- \longrightarrow C_6H_5CH_2NO_3 \quad (11)$$

$$C_6H_5CH_2^+ + H_2O \longrightarrow C_6H_5CH_2OH + H^+ \quad (12)$$

It is interesting to speculate on the possibility that the transient yellow color observed when the reaction is run in high concentration (see experimental part) is that of benzyl ion.

Since reaction (11) is subject to a large salt effect, and reaction (12) to a small one, the effect of added inorganic nitrates upon the distribution will not be a simple one. The fraction R of the product which is benzyl alcohol is easily shown to be given by the equation

$$R = 1/\left(1 + \frac{k_1}{k_2}[NO_3^-]f_1^2\right)$$

where k_2 and k_1 are rate constants for the reaction of benzyl ion with nitrate ion and with water, respectively, and f_1 is the activity coefficient of a singly charged ion. Addition of nitric acid or a nitrate increases (NO_3^-) but decreases f_1. In view of the incompletely ionized nature of mercuric nitrate and the low dielectric constant of the medium, it is hopeless to attempt to predict the value of f_1. Qualitatively, however, we do find that the rate of change of distribution with nitrate concentration is considerably smaller than that given by the assumption that f_1 is constant. It is rather surprising that the divalent nitrates fall on the same curve. The salt effect also accounts for the fact that the proportion of benzyl alcohol rises to 88.6% when perchlorate is added to the reaction mixture of mercuric nitrate and benzyl chloride.

We have assumed that a wide variety of mercuric compounds can react with alkyl halides by virtue of the tendency of mercuric ion to form stable compounds with chloride ion. Neglecting the dioxane-solvated compounds, the possibilities in this reaction are $Hg(H_2O)_4^{++}$, $Hg(H_2O)_3(NO_3)^+$, $Hg(H_2O)_2(NO_3)_2$, $Hg(H_2O)_3Cl^+$, $Hg(H_2O)_2ClNO_3$, $Hg(H_2O)_3(ClO_4)^+$, $Hg(H_2O)_2(ClO_4)_2$ and $Hg(H_2O)_2Cl(ClO_4)$. Further, Nicolet and Stevens[11] report that the alcoholysis of alkyl halides is accelerated by the corresponding mercuric halides, the mercuric halide being inactivated according to the equation $HgX_2 + 2X^- \rightleftarrows HgX_4^=$. These considerations result in a picture analogous to that of the generalized acid catalysis proposed by Brönsted.[12] If this is true, the velocity of reaction of each of these mercury compounds with alkyl halides should be a function of their tendency to combine with chloride ion as measured by equilibrium constants.

The hypothesis of a carbonium ion as an unstable intermediate has been used successfully to explain a variety of rearrangement reactions.[13] Such ions are certainly not set free in all reactions of substitution; they are very improbable intermediates for reactions of the type of equations (1) and (2). But it seems likely that they appear in many of the reactions of organic halogen compounds with mercuric and silver salts, and with other metallic salts which have a strong affinity for halogen ion.[14] A carbonium ion intermediate is also very probable in the many condensation and other reactions of hydroxyl compounds in which the very strong acid sulfuric is used as condensing agent. Here the driving force must be taken to be the energy of formation of water or of oxonium ion instead of the energy of linkage of metallic ion with chloride ion.

The process of formation of the carbonium ion in these cases may be considered to be a case of the London three-body substitution mechanism, just as much as is the reaction of iodide ion with an alkyl chloride, the type being

$$A + BC \longrightarrow AB + C \quad (13)$$

$$I^- + RCl \longrightarrow IR + Cl^- \quad (14)$$

$$Hg^{++} + ClR \longrightarrow HgCl^+ + R^+ \quad (15)$$

The reaction of equation 14 may be called a sub-

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(11) Nicolet and Stevens, THIS JOURNAL, **50**, 135 (1928).

(12) Brönsted, *Chem. Rev.*, **5**, 231 (1928).

(13) (a) Lowry, *Chemistry and Industry*, **43**, 1128 (1924); (b) Meerwein, *Ann.*, **453**, 16 (1927); (c) Whitmore, THIS JOURNAL, **55**, 4153 (1933).

(14) (a) Meerwein and Van Emster, *Ber.*, **55B**, 2500 (1922); (b) Bodendorf and Boehme, *Ann.*, **516**, 1 (1935).

stitution on carbon, that of equation 15 a substitution on halogen.

Experimental

Materials and Solutions.—The preparation and purification of primary standard mercuric oxide have been described previously.[8] C. P. mercuric nitrate was used directly. All other metallic salts were purified by the usual methods. Reagent grade concentrated nitric acid and 20% perchloric acid were used. Benzyl chloride (Mallinckrodt Analytical Reagent) was fractionated *in vacuo*, the middle third (b. p. 56–58° at 4–5 mm.; $n^{25}\text{D}$ 1.5363) being taken for kinetic experiments. Benzyl alcohol (Eastman Kodak Co.) was fractionated *in vacuo*, the middle third being taken; b. p. 77–78° at 4–5 mm. Benzyl nitrate was prepared by the method of Nef.[15] After two fractionations *in vacuo*, the material gave a negative test for chloride on long standing with alcoholic silver nitrate, b. p. 100–101° at 18 mm. Dioxane was purified by a modification of the method of Kraus and Vingee.[16] The sample was refluxed with solid sodium hydroxide until there was no further resin formation. After filtering, it was refluxed with metallic sodium for about six hours and distilled; b. p. 101.1–101.3° at 760 mm. On standing for several days this dioxane develops an impurity which slowly reacts with mercuric nitrate forming mercurous salt; this error was found to be negligible under the conditions of the kinetics.

Mercuric nitrate solutions were prepared both by dissolving mercuric nitrate in nitric acid and by dissolving mercuric oxide in nitric acid with consistent results. Mercuric perchlorate solutions were made up from primary standard mercuric oxide and perchloric acid. The preparation of all other standard solutions already has been described.[8]

Kinetic Experiments.—The details of the titration method for following the reactions have been discussed elsewhere.[8] Into a 300-cc. glass-stoppered bottle was pipetted the appropriate quantity of dioxane and water (or water solution of the other substance to be added). After weighing in the benzyl chloride from a weight buret, the bottle was set into the thermostat at 24.65 ± 0.01° for at least thirty minutes. The reaction was then started by pipetting in 5 cc. of standard mercuric nitrate prepared so as to give the desired concentration. At measured intervals, 10 cc. of the reaction mixture was delivered into 5 cc. of standard 0.1 *N* potassium chloride, thus effectively killing the reaction. The acidity was then titrated with 0.025 *N* sodium hydroxide to a brom phenol blue end-point. After the addition of 4 cc. of 0.2 *N* nitric acid to bring the solution to optimum acidity, and 5 drops of diphenylcarbazide indicator, the excess chloride present was titrated with 0.02 *N* mercuric nitrate. Thus, only one titration mixture was necessary to determine both the nitric acid produced and the mercuric nitrate used up in the reaction.

The initial mixing of the mercuric nitrate solution with the rest of the reaction mixture caused a momentary rise in temperature; the error was negligible except for the very fast runs, in which case the standard mercuric nitrate solutions were made up in 50% dioxane by volume, thus cutting down the heat of mixing.

Only calibrated weights and volumetric apparatus were used. In calculating velocity constants, the volume which in practically all runs was about 100 cc. was corrected for the shrinkage on mixing dioxane and water. Since one mole of mercuric nitrate reacts with two moles of benzyl chloride, the usual equation for a bimolecular reaction must be modified to

$$k = \frac{2}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

in which the quantities a and b are the concentrations in *equivalents* per liter of mercuric nitrate and benzyl chloride, respectively. The maximum error in any one constant is about 2%; the precision generally found was 1% or better.

Table VII shows the types of kinetics found under various conditions. In three runs presented the initial concentrations of mercuric nitrate and benzyl chloride were both 0.025 *N*. Experiment 66 performed in 75% dioxane by volume, shows the downward drift found in that medium. In 60% dioxane expt. 61 shows the second order constant found with a high concentration of nitrate ion, while with expt. 45, with only a small concentration of added nitrate, a small upward drift in the constants was found.

TABLE VII

TYPES OF KINETICS FOUND

t, min.	Expt. 66 $a - x^a$	k
0	0.02474	...
10	.02358	0.398
30	.02173	.374
91.3	.01761	.358
180	.01400	.344
270	.01159	.340
	Expt. 61	
0	0.02525	...
10	.02222	1.080
30	.01792	1.080
60	.01381	1.094
105	.01046	1.066
150	.00831	1.080
	Mean	1.080
	Expt. 45	
0	0.02505	...
10	.02225	0.924
30	.01837	.968
60	.01442	.980
120	.01015	.976
150	.00869	1.002
180	.00760	1.018

[a] $a - x = (\text{Hg(NO}_3)_2) = (\text{BCl})$, in equivalents per liter, at the time t.

Representative data on the distribution of products are presented in Table VIII. It can be seen that the distribution of products is a constant throughout the reaction.

Products of the Reaction.—In order to obtain enough material to separate and identify the products, the reaction

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[15] Nef, *Ann.*, **309**, 171 (1889).

[16] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

TABLE VIII

DISTRIBUTION OF PRODUCTS IN 60% DIOXANE—EXPT. 49

Concn. NaOH solution/concn. $Hg(NO_3)_2$ solution = 1.075

t, min.	Acid titer, cc.	$Hg(NO_3)_2$ titer, cc.	100R (%BOH)
30	2.33	2.89	86.6
60	3.70	4.60	86.4
90	4.63	5.69	87.5
120	5.20	6.44	86.7
180	5.87	7.40	85.2
24 hrs.	7.73	9.69	86.5
		Mean	86.5

was run at 1.0 *N* concentrations in a volume of 500 cc. To a solution of 60 cc. (0.5 mole) of benzyl chloride in 300 cc. of dioxane was added a solution of 70 g. (0.65 equiv.) of mercuric oxide in 100 cc. of water and 55 cc. of concentrated nitric acid. After standing for a few minutes mercuric chloride crystallized out and the solution developed a yellow color which disappeared after about forty-five minutes. Twenty-four hours later the mercuric chloride was filtered off and solid potassium chloride was added to convert excess mercuric nitrate to mercuric chloride. Enough sodium bicarbonate was added to neutralize most of the nitric acid. The filtered solution was then extracted twice with ether and the combined ether layers distilled *in vacuo*. The first fraction containing ether, dioxane and a little nitric acid was discarded. The second fraction, b. p. 96–106° at 22 mm., was colorless and had the aromatic odor of benzyl nitrate; no higher boiling fraction was obtained.

That the second fraction was a mixture of benzyl alcohol and benzyl nitrate was proved in the following way.

A portion of the mixture gave a dinitrobenzoate, m. p. 112° after three recrystallizations. Known benzyl dinitrobenzoate melts at 112.5°; mixed melt, 112°. Pure benzyl nitrate alone will not react with dinitrobenzoyl chloride.

The fraction gave a strong nitrate test (diphenylamine) but the nitrate could not be extracted with water. A few cc. was boiled with strong sodium hydroxide for ten minutes, and the excess alkali neutralized with hydrochloric acid. After extracting several times with ether to remove organic material, the water layer gave a strong test for nitrate. The presence of a nitrate ester with the same boiling point as benzyl nitrate was thus proved.

No attempt was made to isolate the products of the mercuric perchlorate reaction because of the explosive nature of perchlorates in the presence of organic matter.

Isolation of the Retardant Compound.—After setting up a reaction mixture as described above, the various extracts, wherever practicable, were tested for their effect on the rate of the mercuric nitrate–benzyl chloride reaction in 75% dioxane. After pumping off the ether and dioxane, 5 cc. of the residue (I) (almost entirely benzyl alcohol, benzyl nitrate and mercuric chloride) was found to lower the velocity constant from 0.396 to 0.110. This residue was extracted with dilute sodium hydroxide; upon addition of hydrochloric acid to the sodium hydroxide layer, a white crystalline compound (II) precipitated. After completely extracting I with dilute sodium hydroxide, the organic layer (III) was washed twice with water, once with 0.2 *N* nitric acid, and once more with water. The washed residue (III) had no retarding effect, showing that the only retardant was the alkali soluble material.

A small portion of the white precipitate (II) was insoluble in hot water; its amount was too small for study. The yield of water-soluble material after four recrystallizations (once with norite) from water was 200 mg., m. p. 126–126.5°. Fifty mg. of the compound produced a retardation from 0.396 to 0.370.

Although the reaction is almost complete in a few hours, the fact that only small amounts of the compound are obtained if the reaction mixture is not allowed to stand overnight, indicates that it is formed by a secondary reaction. It was then found that the compound could also be prepared by allowing mercuric nitrate to stand with benzyl alcohol in dioxane–water, using the same method of extraction. Allowing the other products of the reaction to stand together or with mercuric nitrate gave no result. It thus appears that the retardant compound is formed solely by a slow reaction of mercuric nitrate and benzyl alcohol in these media.

The compound itself is a new one and answers to the empirical formula of a chloro-mercuri benzyl alcohol. This is surprising in view of its acidic nature, and its structure is now being investigated further. Calcd. for C_7H_7OHgCl: acid eq., 343; C, 24.49; H, 2.04. Found: acid eq., 345; C, 24.52, 24.47; H, 1.69, 1.99.[17]

Summary

The rate of the reaction of mercuric nitrate with benzyl chloride and the distribution between the two major products, benzyl nitrate and benzyl alcohol, have been studied in dioxane–water mixtures of various proportions. The effects of the addition of nitrates, of perchlorates and of mercuric chloride upon both rate and distribution have been investigated, and kinetic complications due to a slow secondary reaction have been unraveled. A two-step mechanism involving non-ionized mercuric nitrate as the principal reactant and benzyl ion as an intermediate has been shown to be extremely probable.

NEW YORK, N. Y.

RECEIVED MARCH 23, 1937

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[17] We are indebted to Dr. D. Price and Mr. S. Gottlieb for these analyses.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Rare Earth Metals and their Compounds. I. The Binary System Hexahydrated Lanthanum and Magnesium Nitrates

BY LAURENCE L. QUILL AND RICHARD F. ROBEY

Although the reality of the existence of the rare earth double nitrates is supported by a multitude of early accumulated evidence, some doubt has been cast by the more recent work of di Capua.[1] In an endeavor to clarify the question a series of investigations on binary and ternary systems containing salts of the rare earth elements has been undertaken. The first results of these investigations, consisting of the thermal analysis of the system hexahydrated lanthanum and magnesium nitrates, are herein reported.

Experimental

The magnesium salt was prepared from Baker and Adamson "C. P. Reagent" magnesium nitrate employing the procedure of Ewing and others.[2] The lanthanum was originally purchased as a "pure" oxide from the Maywood Chemical Co. This oxide was mixed with pure magnesium oxide in the ratio 1 mole to 3.1 moles, dissolved in nitric acid, and fractionally crystallized in a series of a constant number of fractions for at least fifty times. A middle fraction of the series finally was chosen as the purest for the intended purpose. The magnesium was removed by repeated precipitation of the lanthanum oxalate in acid solution, washing, ignition, solution. Ultimately the nitrate was crystallized from the nitric acid solution, twice from water, and dried over 55% sulfuric acid in a desiccator. A 20-cm. layer of a sirupy solution of the nitrate showed no absorption spectrum of the didymium elements. The arc emission spectrum gave no indication of the presence of any of the rare earth elements other than lanthanum.

The experimental method was that used by other investigators in similar systems.[2] Briefly it consisted of heating the mixtures in Pyrex glass tubes inserted in a well-stirred oil-bath to a temperature somewhat above their melting points. The constantly stirred mixtures were then permitted to cool, the rate of cooling being determined by means of a thermometer. The thermometer was comparatively calibrated with a Bureau of Standards certified instrument. The temperature difference between the mixtures and the bath was always kept as small as possible.

TABLE I

CRYSTALLIZATION TEMPERATURES: THE SYSTEM LANTHANUM AND MAGNESIUM NITRATE HEXAHYDRATE

$La(NO_3)_3{:}6H_2O$ wt., %		Temp., °C.
0.0		89.7
5.0		88.5
...	(Eutectic I)	88.0
10.0		91.0
20.0		101.7
30.0		107.7
40.0		111.5
50.0		113.2
60.0		110.8
67.2		110.6
70.0		107.8
78.0		101.6
90.0		76.5
95.0	(Eutectic II)	64.7
100.0		66.5

Results.—The data of Table I have been derived from time-differential temperature cooling curves of the various mixtures. Slight losses of water were noted, especially among the higher melting mixtures on repeated determination.

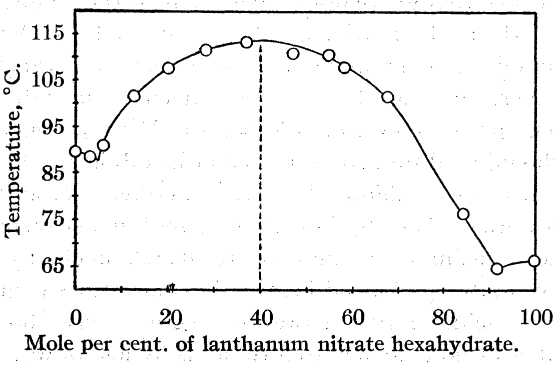

Fig. 1.—Liquidus of the system hexahydrated lanthanum and magnesium nitrates.

The observed temperature points have been plotted in Fig. 1 against the mole percentage composition. The melting point of the magnesium nitrate (89.7°) agrees well with that already recorded in the literature (89.9°);[2] the melting point of the lanthanum nitrate (66.5°) is slightly higher than that for the *beta* form (65.4°), as reported by Friend.[3] The type of the liquidus curve confirms the formation of a compound by these nitrates with the ratio $2La(NO_3)_3{:}3Mg(NO_3)_2$. A comprehensive study of the ternary system rare earth metals–magnesium nitrates–water is being conducted at the present time.

COLUMBUS, OHIO

RECEIVED APRIL 12, 1937

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[1] C. di Capua, *Gazz. chim. ital.*, **59**, 164–169 (1929).

[2] W. W. Ewing, J. D. Brandner, C. B. Slichter and W. K. Griesinger, THIS JOURNAL, **55**, 4822–4824 (1933).

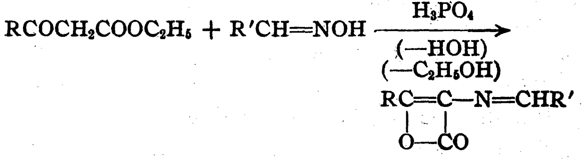
[3] J. N. Friend, *J. Chem. Soc.*, 824 (1935).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

A Synthesis of Arylidene Isoxazolones[1]

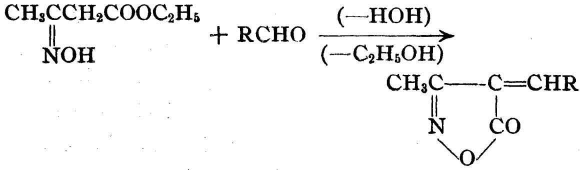
BY JOHN J. DONLEAVY AND EVERETT E. GILBERT

In 1928–1929 G. Minunni and others published a series of papers[2–4] in which a reaction between aromatic aldoximes and beta keto esters was investigated. The interaction of these substances in the presence of phosphoric acid was described as leading to the formation of alpha arylidene crotonic acid lactones in the case of acetoacetic ester, and alpha arylidene cinnamic acid lactones in the case of benzoyl acetic ester



A careful study of their conditions of experiment and a consideration of the structures assigned to the reaction products led the writers to believe that grave doubt existed as to the validity of their observations. As formulated by Minunni these products are beta lactones, which experience[5] has shown to be extremely unstable. The presence of a double bond in these products should tend toward even greater instability. The substances exhibit, however, marked stability toward acids since they are prepared in a strongly acid medium and may be recovered unchanged even after prolonged heating in concentrated sulfuric acid. Furthermore, oximes as a class show little or no tendency to form anils by loss of water in reaction with activated hydrogens. Finally, beta keto esters as a class have never been observed to condense in the sense of beta lactone formation.

As a result of these conclusions, the work of Minunni and his collaborators has been repeated in its entirety. The striking similarity of the products obtained in this way to those obtained by R. Schiff and M. Betti[6] by treating acetoacetic ester oxime or its anilide with various aromatic aldehydes led to the thought that the substances obtained by Minunni might be isoxazolones of the same type as those obtained by Schiff and Betti. The corresponding methylisoxazolones were accordingly prepared by the independent



method of Schiff and Betti, and upon comparison proved to be identical with the products obtained by Minunni. In the case of the phenylisoxazolones derived from benzoylacetic ester, we have treated the aldehydes directly with 3-phenylisoxazolone-5 according to the technique developed by A. Wahl and A. Meyer.[7] These are also identical with the corresponding products obtained by Minunni from benzoylacetic ester and aromatic aldoximes.

As a result of the above observations it is now established beyond any reasonable doubt that the products described by Minunni and his coworkers as alpha arylidene amino lactones are in fact arylidene isoxazolones.

Minunni further studied the behavior of his so-called lactones with phenylhydrazine and with warm dilute alkali. By using his method of treatment we have obtained products with the properties and with the empirical formulas he has described; however, these reaction products also arise from the corresponding isoxazolones by exactly the same course of treatment. In this way we have proved that both the parent substances and the derivatives must have very different structures from those originally assigned by him.

In a typical case he treated what we now know to be 3-phenyl-4-benzylidene-isoxazolone-5 with phenylhydrazine (2 moles) and obtained what he termed α-amino-β-hydroxycinnamic acid phenylhydrazide. We have found this to be the phenylhydrazine salt of 3-phenylisoxazolone-5; it is identical with the salt obtained directly from 3-phenylisoxazolone-5 by the action of phenylhydrazine

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(1) This communication describes work done by Everett E. Gilbert in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) G. Minunni and S. D'Urso, *Gazz. chim. ital.*, **58**, 485 (1928); *C. A.*, **23**, 1120 (1929).

(3) G. Minunni, S. D'Urso, V. Bellecci, and I. Ottaviano, *Gazz. chim. ital.*, **59**, 32 (1929); *C. A.*, **23**, 3676 (1929).

(4) G. Minunni, I. Ottaviano, and V. Spina, *Gazz. chim. ital.*, **59**, 116 (1929); *C. A.*, **23**, 3914 (1929).

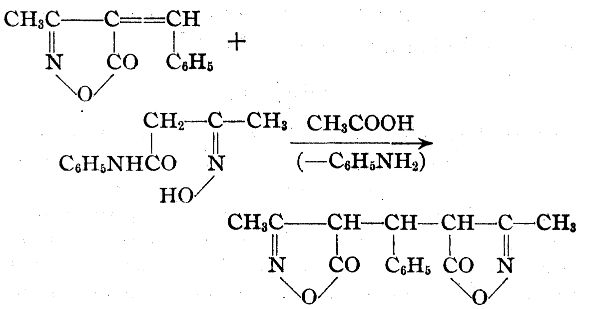
(5) H. Staudinger, "Die Ketene," Stuttgart, 1912, p. 60.

(6) R. Schiff and M. Betti, *Ber.*, **30**, 1337 (1897).

(7) A. Wahl and A. Meyer, *Bull. soc. chim.*, [4] **3**, 952 (1908).

by the method described by R. Uhlenhuth.[8] (In the case of the arylidene isoxazolones, the corresponding aldehyde phenylhydrazone was also formed.)

We have found the action of alkali on these compounds to be specific for each compound. On treating 3-methyl-4-benzylidene-isoxazolone-5 with hot aqueous 5% sodium carbonate, Minunni obtained a product which he made no attempt to analyze or identify. We have obtained a product agreeing with the physical properties he has cited. It also agrees in every way with a product originally obtained by Schiff and Betti[6] by alkaline hydrolysis of the isoxazolone. They tentatively proposed the structure I. We have also produced this compound by the action of phenylhydrazine on the parent substance under mild conditions. Minunni obtained it from the parent substance by the mild action of hydroxylamine. He also corroborated Schiff and Betti's observation that exactly half a mole of benzaldehyde was removed per mole of product formed. We have also been able to synthesize this product by treating acetoacetic ester oxime anilide with 3-methyl-4-benzylidene-isoxazolone-5 in glacial acetic acid.



I

We have also found it possible to prepare a new diethyl derivative of this substance. However, all attempts made by us to synthesize this product by the direct action of hydroxylamine on benzylidene bis-acetoacetic ester resulted in failure because of the practical impossibility of preparing the last-mentioned material in pure form.

On heating 3-phenyl-4-benzylidene-isoxazolone-5 with 10% aqueous sodium carbonate for several hours, we obtained benzaldehyde and 3-phenylisoxazolone-5, which behavior is in marked contrast to that of the methyl analog just discussed. 3-Methylanisylidene-isoxazolone-5 could be reprecipitated unchanged by mineral acid after the above treatment; in cases where Minunni observed more than the melting point, he tended to assign formulas to all the above-mentioned compounds without the support of corroborative data, and often even without analyses.

In an attempt to widen its scope, a further study of the mechanism of the above reaction was made. Condensation will occur in the presence of any strong acid. Minunni used concentrated phosphoric acid of unspecified strength; Schiff and Betti[6] used hydrogen chloride gas or strong aqueous hydrochloric acid. We have found that sulfuric acid of strength from 40 to 60% may be employed. Hydrated oxalic acid may be used to advantage because of its mildness. Concentrated sulfuric acid and concentrated hydrochloric acid tend to produce decomposition into black tarry products. Acetic acid gave no evidence of reaction; several basic catalysts were tried without success. Iodine also gave no reaction. Maximum yields of 65% were obtained in the case of acetoacetic ester by allowing the components to stand for one day at room temperature mixed with 10% of the total weight of 85% phosphoric acid. However, in the case of benzoylacetic ester, heating for three hours at 100° was necessary for condensation to occur. Prolonged heating or too high temperatures tended to reduce the yields and to produce decomposition.

Aliphatic oximes in general we have found to produce viscous glassy polymeric products when applied in the above reaction. Aliphatic and alicyclic ketoximes condensed with poor yields (20%) or not at all.

The mechanism of this reaction appears to be as follows. First hydrolysis of the oxime occurs, liberating the parent aldehyde and hydroxylamine. Formation of the glassy polymers from the aliphatic oximes is due no doubt to the polymerization of the aldehydes in the strongly acid medium. It appears probable that the next step in the reaction is the condensation of the aldehyde with the active methylene group. We believe such to be the case since *n*-butylacetoacetic ester could not be made to take part in the above reaction, even to the extent of forming *n*-butylisoxazolone. The next step consists of the formation of the beta ketoxime by means of the hydroxylamine split out in the first stage and its ring closure to form the isoxazolone ring.

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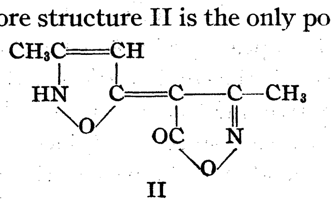
[8] R. Uhlenhuth, *Ann.*, **296**, 44 (1897). The carbonyl group in the isoxazolone ring does not condense in the sense of a ketone. Since isoxazolones as a class are strongly acidic, they form very stable salts with bases. This particular product reduces Fehling's solution, a behavior to be expected from phenylhydrazine salts, but not from phenylhydrazones.

Structure of the Alleged Methylisoxazolone.—Thinking that the methyl arylidene isoxazolones might easily be prepared by condensing an aldehyde with 3-methylisoxazolone-5 (as Wahl and Meyer[7] had done in the case of the 3-phenyl analog), we prepared what was described as this substance by several authors. It was found to be unexpectedly inert toward aldehydes, while the phenyl analog condensed easily under the same conditions. A. Hantzsch[9] had obtained the so-called methylisoxazolone by allowing acetoacetic ester to stand with an equivalent weight of hydroxylamine for several hours in strongly alkaline solution; he cites unconvincing analytical data. A product of identical physical properties was obtained by L. Knorr and B. Reuter[10] by treating acetoacetic ester oxime anilide with strong acids or with strong bases; they cite no analytical data. R. Uhlenhuth[8] prepared an exhaustive series of salts and alkyl derivative of this substance. By a long series of careful analyses (which did not include an analysis of the original substance), he proved that they were all mono derivatives of two methylisoxazolone molecules minus one molecule of water. He made no attempt to propose structures, but merely suggested that methylisoxazolone might be "dimolecular," or that when salt formation occurred, two molecules united with loss of water. A molecular weight determination made by Uhlenhuth agrees well with a dimolecular structure of some sort.

We have resynthesized this substance according to the method of Hantzsch, and on analysis have found it to correspond exactly to a molecule formed from two methylisoxazolone molecules by loss of one molecule of water. Since the alkylation of isoxazolones always occurs on the nitrogen[8] (which exhibits strongly acidic behavior), and since the formation of mono derivatives only has been observed, we have concluded that one of the two rings must lack the necessary hydrogen, and that therefore structure II is the only possible one.



II

The melting points of related isoxazolones found in the literature also preclude any monomolecular structure. 3-Methyl-4-chloroisoxazolone-5 melts at 86°,[11] 3-methyl-4-benzylisoxazolone-5 melts at 106°;[11] other cases could be cited to show that melting points of the 3-methylisoxazolones become higher with increasing molecular weight of the substituent in the 4-position. It is therefore strange that the alleged methylisoxazolone should melt at 169°, a figure higher than any of its recorded 4-substituted derivatives. Methylisoxazolone has accordingly never been prepared. The compound thought by various workers to be this substance was actually "dimethyl-diisoxazolone."

The structure and the autocondensation reaction of methylisoxazolone bear striking similarities to those of gamma-butyrolactone. This lactone is composed of a five-membered ring containing an active methylene group adjacent to an ester grouping; the same is true of the isoxazolone. Butyrolactone also condenses with itself in the presence of alkaline agents to form a "dimolecular" product, water being liberated between a keto and a methylene group. However, it might be expected that methylisoxazolone would condense even more easily in this sense, since its active methylene would be rendered even more active by the possibility of a double bond on the nitrogen (producing activity similar to that found in the methyl group of quinaldine).

Experimental

Preparation of 3-Methyl-4-benzylidine-isoxazolone-5.—One-half mole each of benzaldoxime (60.5 g.) and acetoacetic ester (65 g.) were mixed, and 10% of the total weight of phosphoric acid (12.5 g.) was added with gentle shaking. The mixture was allowed to stand overnight at room temperature. The solid product which separated was then filtered, and successive crops were obtained from the sirupy filtrate by allowing it to stand further. The pure product was obtained in the form of yellow crystals upon recrystallization from benzene. It melted to a clear yellow liquid at 146–147° (corr.). The yield of recrystallized product was 65% of the theoretical (94 g.).

Anal. Calcd. for $C_{11}H_9O_2N$: N, 7.49. Found: N, 7.53, 7.30.

The same isoxazolone was then made by the method of Schiff and Betti[6] from benzaldehyde and acetoacetanilide oxime; glacial acetic acid was used instead of hydrochloric as they suggest. The melting point and physical properties were found to be the same as those of the above compound, and a mixed melting point showed no depression.

3-Phenyl-4-benzylidene-isoxazolone-5.—Equivalent amounts of benzoylacetic ester (19.2 g.) and benzaldoxime (12.1 g.) were condensed in the presence of phosphoric acid (5 g.) by heating for three hours at 100° with occasional shaking. The combined crops of crystals were

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[9] A. Hantzsch, *Ber.*, **24**, 498 (1891).

[10] L. Knorr and B. Reuter, *ibid.*, **27**, 1174 (1894).

[11] R. Schiff and G. Viciani, *ibid.*, **30**, 1159 (1897).

recrystallized from ethanol, and melted to a clear yellow liquid at 193–194° (corr.). The yield of pure product was 48% (12.8 g.).

Anal. Calcd. for $C_{16}H_{11}O_2N$: N, 5.62. Found: N, 5.42, 5.32.

The same isoxazolone was synthesized from phenylisoxazolone and benzaldehyde, using the method described by Wahl and Meyer,[7] 3-phenylisoxazolone-5 being first made by the method of Hantzsch.[9] The crystals were exactly similar to those obtained above. A mixed melting point showed no depression.

3-Phenyl-4-anisylidene-isoxazolone-5.—This compound was synthesized by heating equivalent amounts of benzoylacetic ester (19.2 g.) and anisaldoxime (15.1 g.) with phosphoric acid (5.0 g.) at 100° for three hours. Lemon-yellow needles were obtained from ethanol in a yield of 60% of the theoretical (17.0 g.); it melted at 164–165° (corr.) to a clear yellow liquid.

Anal. Calcd. for $C_{17}H_{13}O_3N$: N, 5.02. Found: N, 5.07, 5.17.

Yellow crystals exactly similar to those just described were obtained by the method of Wahl and Meyer used above; in this case phenylisoxazolone was condensed with anisaldehyde. A mixed melting point showed no depression. The products were identical.

3-Methyl-4-anisylidene-isoxazolone-5.—Acetoacetic ester (13.0 g.) and anisaldoxime (15.1 g.) condensed in 75% (16.1 g.) yield by being allowed to stand at room temperature in the presence of phosphoric acid (5 g.). On recrystallization from alcohol yellow needles were obtained melting to a clear liquid at 180–181° (corr.). This product has never before been described as such in the literature.

Anal. Calcd. for $C_{12}H_{11}O_3N$: N, 6.45. Found: N, 6.38, 6.68.

3-Methyl-4-isopropylidene-isoxazolone-5.—Acetone oxime (7.3 g.) and acetoacetic ester (13.0 g.) condensed in 20% yield (2.6 g.) on being allowed to stand at room temperature with phosphoric acid. On recrystallization from ethanol white flakes were obtained from ethanol which melted to a clear liquid at 120–121° (corr.). Attempts to obtain further crops failed in this case. This product is identical in properties with that obtained by Schiff and Betti from acetoacetic ester oxime and acetone.[6]

Anal. Calcd. for $C_7H_9O_2N$: N, 10.08. Found: N, 10.03, 10.00.

Cyclohexanoneoxime, acetaldoxime, and heptaldoxime could not be condensed in the above sense. In the last two cases viscous glasses were obtained on allowing the oximes to stand with acetoacetic ester and phosphoric acid. *n*-Butylacetoacetic ester gave no reaction in the above sense even when heated to 120° for one hour; some starting material and its hydrolytic products were recovered.

Preparation of Compound I. Alkaline Hydrolysis of the Isoxazolones.—3-Methyl-4-benzylidene-isoxazolone-5 (15.0 g.) was suspended in 200 cc. of aqueous sodium carbonate solution. This was kept at 70° until solution was complete (about one hour). During this time benzaldehyde collected on the surface in an oily layer. The solution was cooled, and ether extracted to remove benzaldehyde. It was then acidified strongly with dilute hydrochloric acid. A gum separated which always crystallized on trituration with the acid. The crystals were filtered and washed with dilute acid. The yield of crude product was 90% of the theoretical (9.6 g.). It may be recrystallized from hot water, observing precautions to carry out the operation at maximum speed since the compound decomposed to red products if heated for a prolonged period at the temperature of boiling water. It was a yellow powder, melting with decomposition and effervescence to a red liquid at 150–151° (corr.). If it was recrystallized from ethanol, it separated as a white powder which turned pink and then yellow on exposure to the air. However, the compound crystallized only with difficulty from this solvent. The product was soluble in bases and could be reprecipitated on acidification with mineral acids. It was slightly soluble in cold water, quite soluble in hot water. Its water solution was acid toward litmus.

Anal. Calcd. for $C_{15}H_{14}O_4N_2$ (as in formula I): N, 9.79. Found: N, 9.82, 9.82.

The same hydrolysis product was obtained from samples of 3-methyl-4-benzylidene-isoxazolone-5 made both by Minunni's method and by the method of Schiff and Betti. A mixed melting point showed no depression.

A compound identical with the hydrolysis product just described was prepared by a new and independent method. One gram of 3-methyl-4-benzylidene-isoxazolone-5 was dissolved in glacial acetic acid and 1 g. of acetoacetanilide oxime was then added with shaking. It went into solution with evolution of heat and on standing for several hours yellow prisms formed. One recrystallization from glacial acetic acid and one from hot water gave a product melting as above. The yield was 1.1 g. or 69% of the theoretical. A mixed melting point with the above compound showed no depression.

To prepare its diethyl derivative, 10 g. of the above compound was dissolved in 5% aqueous sodium carbonate. Slightly more than two molecular quantities of diethyl sulfate (11.0 g.) were added and the mixture was shaken at room temperature for twelve hours. It was then extracted three times with ether. On evaporation of the ether, white prisms were obtained, which were recrystallized from alcohol. It melted to a clear colorless liquid at 159–161° (corr.). The yield was 50% of the theoretical (6.0 g.).

Anal. Calcd. for $C_{19}H_{22}O_4N_2$: N, 8.19. Found: N, 8.0, 8.04.

3-Phenyl-4-benzylidene-isoxazolone-5 was dissolved in excess 10% aqueous sodium carbonate and heated for three hours on a boiling water bath. On acidification a gum formed, which crystallized on trituration. Recrystallized from benzene, the product showed no definite melting point, but began to soften at 120°, finally melting with decomposition to a red liquid at about 155°. A mixture of phenylisoxazolone and phenylbenzylideneisoxazolone showed the same melting phenomena. Final proof that the product was a mixture of the two was obtained by refluxing it with excess benzaldehyde in glacial acetic acid solution. The solid which formed on pouring into water was washed with a little ethanol. Without further purification it melted at 191–192°, forming a clear yellow liquid, showing that it was pure 3-phenyl-4-benzylidene-isoxazolone-5. Minunni obtained 3-phenylisoxazolone-5 from 3-phenyl-4-benzylidene-isoxazolone-5, but he considered it to be alpha-aminocinnamolactone, a compound which would have the same empirical formula.

Reaction with Phenylhydrazine.—The salt was prepared directly from 3-phenylisoxazolone and phenylhydrazine by the method described by Uhlenhuth.[8] It can be recrystallized in the form of white flakes from methanol; it melts with decomposition to a red liquid at 153–154°. The yield was quantitative. It easily reduced Fehling's solution, showing it to be a phenylhydrazine salt and not a phenylhydrazone. The same salt (plus the corresponding aldehyde phenylhydrazone) was obtained by mixing warm methanol solutions of 3-phenyl-4-benzylidene-isoxazolone-5 (1 mole) and phenylhydrazine (2 moles); the same was done with 3-phenyl-4-anisylidene-isoxazolone-5. The aldehyde phenylhydrazones were separated from the salt in each case by taking advantage of the greater solubility of the former in warm benzene. Mixed melting points showed no depression, and salts from the varying sources showed identical analyses.

Anal. Calcd. for $C_{15}H_{15}O_2N_3$: N, 15.61. Found: N, 15.52, 15.76.

When 3-methyl-4-benzylidene-isoxazolone-5 was treated as above, a 50% yield of compound II was obtained, plus benzaldehyde phenylhydrazone.

Preparation of Dimethyl-diisoxazolone.—The method of Hantzsch[9] was employed using 65.0 g. acetoacetic of ester. On recrystallization from ethanol a 33% yield (17.1 g.) of white flakes was obtained. It melts with decomposition to a red liquid at 168–169° (corr.).

Anal. Calcd. for $C_8H_8O_3N_2$: N, 15.56. Found: N, 15.58, 15.58.

Summary

1. It is shown that aromatic aldoximes and beta keto esters react in the presence of acids to form arylidene isoxazolones, and not arylidene amino lactones as previously reported.[2–4]

2. The action of phenylhydrazine and of an alkaline hydrolytic agent has been studied, and the earlier work has been corrected and extended.

3. The optimum conditions for condensation have been found. The probable mechanism of the reaction is discussed. It has been found that reaction occurs in the presence of strong acids in general.

4. An unsuccessful attempt was made to extend the reaction to aliphatic and alicyclic aldoxime and ketoximes. Acetone oxime did condense, however.

5. It is shown that the compound reported as 3-methylisoxazolone-5 in the literature has actually never been prepared. The product reported as such was actually dimethyldiisoxazolone. Its structure is demonstrated.

NEW HAVEN, CONN. RECEIVED MARCH 27, 1937

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Two Forms of Anhydrous *l*-Rhamnose and a New Method for the Preparation of Crystalline β-Tetraacetyl-*l*-rhamnose[1]

BY ERNEST L. JACKSON AND C. S. HUDSON

l-Rhamnose usually crystallizes as a monohydrate of its α-modification having an initial specific rotation in water of −7.7°, which becomes constant at +8.9° after mutarotation is complete. This form is usually regarded as the configurational analog of α-*d*-mannose of initial rotation +30°, its final value being +14°. In 1895 Emil Fischer[2] crystallized a new form of rhamnose, anhydrous crystals of initial rotation about +31° which is regarded as β-rhamnose, the analog of β-*d*-mannose of initial rotation −17°. Minsaas[3] on repeating Fischer's preparation recently found "about +44°" as the initial rotation, and mentioned that the yield of this anhydrous form is small. We also had been engaged in studying this form and in devising methods for obtaining it in higher yields; our β-rhamnose showed +38° as the initial specific rotation.[4] After the publication of Minsaas' article we repeated our work and again obtained +38° for crystals which by appearance seemed to be of one form only. In the course of the preparation of these β-rhamnose crystals another anhydrous form of quite different crystalline appearance frequently separated. This third form of the sugar shows an initial rotation of about +14°, mutarotating in water at the

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. Presented before the Division of Organic Chemistry, at the Pittsburgh meeting of the American Chemical Society, Sept. 7–11, 1936.

[2] Fischer, *Ber.*, **28**, 1162 (1895); **29**, 324 (1896); Tanret, *Compt. rend.*, **122**, 86 (1896); Purdie and Young, *J. Chem. Soc.*, **89**, 1194 (1906).

[3] Minsaas, *Kgl. Norske Videnskab. Selskabs Forh.*, **6**, 177 (1933); *Chem. Zentr.*, **105**, I, 2738 (1934).

[4] Except where otherwise specified, all rotations in this article are specific rotations at 20° for sodium light.

same rate as the two other forms to the equilibrium value +8.9°. It is apparently a true chemical individual in the crystalline state. Its formula, on the assumption that its components are the known α- and β-forms, is α,β-rhamnose if the rotation of β-rhamnose is +38° (our value), or $3\alpha,2\beta$-rhamnose if the rotation of β-rhamnose is +44° (Minsaas' value). This is the second sugar for which a molecular combination of α- and β-forms in the crystalline state has been found; the other sugar, α,β-lactose, has been described by Hockett and Hudson.[5]

For a long period of years it was not possible to obtain a crystalline tetraacetate of rhamnose. In 1920 Fischer, Bergmann and Rabe[6] showed that crystalline β-tetraacetylrhamnose can be prepared in an indirect way through acetobromorhamnose. It is now shown that the acetylation of β-rhamnose with acetic anhydride and pyridine at low temperature gives a high yield (about 90%) of this crystalline β-tetraacetate. Since β-rhamnose may now be prepared in 85–90% yield from ordinary α-rhamnose hydrate, the present directions furnish the best way of obtaining the crystalline β-tetraacetate. The similar acetylation of α,β-rhamnose gives, besides a sirup, a 43% yield of the β-tetraacetate, which confirms the presence of the β-sugar as one component; the other constituent is presumably α-rhamnose, the tetraacetate of which is known only as a sirup.

Experimental

Dehydration of Rhamnose Monohydrate with Barium Monoxide.—A solution of 50 g. of pure rhamnose hydrate in 2 liters of pure acetone was refluxed with 100 g. of barium monoxide for two hours with exclusion of atmospheric moisture, the barium oxide was filtered off and the drying was repeated with fresh barium monoxide for three and one-half hours. The filtered solution, concentrated to about 700 cc. and kept overnight at 25°, deposited long prismatic needles (32.5 g.); the yield was increased to 40.3 g. (90%) by further concentration of the mother liquor. The crops rotated +8.5 to +10.3° (three minutes) in water and +8.9° (constant). On recrystallization from acetone, which had been dried by refluxing over barium monoxide, the initial rotation increased to an approximately constant value. In the course of three successive recrystallizations and drying in an evacuated desiccator over calcium chloride, the extrapolated initial rotation in water was respectively +13.2, +14.2 and +14.6°. The crystals from each recrystallization were characteristic long primatic needles with m. p. 112.5–113.5° (corr.) and rotation +8.9° (constant) in water.

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.88; H, 7.37. Found:[7] C, 44.18, 44.13; H, 7.44, 7.36.

These crystals of α,β-rhamnose, from their appearance and repeated preparation with the same physical constants, might be mistaken for a homogeneous crystalline isomer of the sugar. Tanret[8] obtained crystals ($[\alpha]_D$ +10.1°) which may be the same as those here described; if so, he was mistaken in their identification, as is now generally recognized, since he considered his product to be anhydrous β-rhamnose.

Dehydration with Absolute Ethanol.—A solution of 10 g. of pure rhamnose hydrate in 25 cc. of absolute ethanol was concentrated on the steam-bath to a sirup. After repeating the process the sirup was crystallized by stirring it with 25 cc. of cold dry acetone, the solvent was evaporated on the steam-bath and the crystals were boiled thrice with 10-cc. portions of dry acetone. Recrystallization from 250 cc. of dry acetone gave long prismatic needles (4 g.) showing the extrapolated initial rotation +14.4° in water and +9.0° (constant); m. p. 112.5–113.5° (corr.). Concentration of the mother liquor increased the yield to 7.7 g. (85%).

After seeds of the two forms of anhydrous sugar were available, either form could be prepared by seeding the acetone solution of the crude dry sugar with the appropriate crystals.

β-Rhamnose.—The conversion of crystals of the lower rotating form (+14°) into the β-sugar was accomplished by adding some crystals of the β-form (fine needles) to an acetone solution from which a considerable quantity of long prismatic needles had separated, and keeping it tightly stoppered at 20° for several weeks when the prismatic needles had changed to clusters of fine needles showing an initial rotation of +37.9° in water. The conversion was effected more rapidly[9] by seeding the acetone solution of the lower rotating form with crystals of β-sugar. Samples of β-rhamnose for analysis and mutarotation were recrystallized twice from dry acetone and dried in a high vacuum at 76° in the presence of phosphorus pentoxide; m. p. 123.5–124.5° (corr.); extrapolated initial rotation +38.4° ($k_1 + k_2 = 0.045$ in minutes and decimal logarithms) in water at 20 ± 0.5° (*c*, 2.24).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.88; H, 7.37. Found:[10] C, 44.09; H, 7.19.

Acetylation.—To a mixture of 8 cc. of acetic anhydride and 8 cc. of pyridine at −12° was added 1.6 g. of powdered β-rhamnose of initial rotation +37.7°. It was shaken at −12° until the sugar dissolved, kept overnight at 0° and poured into 150 cc. of ice and water. After partial neutralization of the solution with sodium bicarbonate, the tetraacetate, which crystallized readily, was filtered off, washed with ice water and dried at 25° *in vacuo* over calcium chloride; weight 2.2 g., rotating +12.7° in chloroform. An additional 0.65 g. of crystals rotating +11.2° (yield, 89%) was obtained from the filtrate by thorough extraction with chloroform, followed

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[5] Hockett and Hudson, THIS JOURNAL, **53**, 4455 (1931).

[6] Fischer, Bergmann and Rabe, *Ber.*, **53**, 2362 (1920).

[7] By Dr. F. H. Goldman.

[8] Tanret, *Bull. soc. chim.*, [3] **15**, 203, 349 (1896).

[9] In occasional experiments, probably because of the presence of seeds of the lower rotating form, it was necessary to repeat the operation.

[10] By Dr. R. T. K. Cornwell.

by washing the chloroform solution twice with 3% hydrochloric acid, once with dilute sodium bicarbonate solution, and crystallization of the sirup, recovered from the dried extract, from ether–petroleum ether at 0°. After one recrystallization from 90% ethanol, the acetate rotated +13.4° in chloroform and melted at 98.5–99° (corr.) alone or mixed with pure β-tetraacetate prepared from β-triacetylrhamnose by the directions of Fischer, Bergmann and Rabe,[6] whose method gave a product rotating, after purification, +13.3° in chloroform (*c*, 3.87) and +14.2° in acetylene tetrachloride compared with their $[\alpha]^{16}_D$ +13.75° in the latter solvent.

The lower rotating form of anhydrous rhamnose was acetylated as described for the β-sugar. One gram of sugar with initial rotation +13.2° yielded 0.85 g. (43%) of β-tetraacetate, most of which melted at 97–98° (corr.) and rotated +12.5° in chloroform. The remainder of the product was a sirup.

Summary

Anhydrous rhamnose, hitherto obtainable only in small yield, has been prepared in 85–90% yield by two methods. The initial rotation of Fischer's β-rhamnose was found to be +38° in water; Minsaas recently reported about +44°. During the preparation of β-rhamnose a second form of the anhydrous sugar rotating about +14° in water frequently separated; this substance appears to be a molecular compound having the composition α,β-rhamnose if the rotation of β-rhamnose is +38° or 3-α,2-β-rhamnose if it is +44°. The presence of the β-isomer as one component of this molecular compound is confirmed by the preparation from it of crystalline β-tetraacetylrhamnose in 43% yield. Acetylation of β-rhamnose yields about 90% of the crystalline β-tetraacetate, which is now best obtained in this way.

WASHINGTON, D. C. RECEIVED APRIL 24, 1937

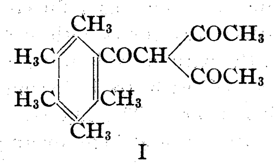
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Acetopentamethylbenzene[1]

BY LEE IRVIN SMITH, ISABELLA M. WEBSTER AND CYRUS GUSS

In a recent paper, Henri Clément[2] has discussed the properties of pentamethylphenylmagnesium bromide, which was prepared by the entrainment method of Grignard[3] by allowing an equimolecular mixture of bromopentamethylbenzene and ethyl bromide in ether to react with magnesium. Among other reactions discussed by Clément was that between acetyl chloride and pentamethylphenylmagnesium bromide, which was claimed to give acetopentamethylbenzene in 34% yield. This substance was described as crystallizing in small rods which melted at 110°. In view of the work of Kohler and Baltzly[4] and of Smith and Guss[1] upon the behavior toward Grignard reagents of diortho substituted aromatic ketones of the type of acetomesitylene and acetopentamethylbenzene, it seemed very unlikely that any enolizable ketone of this type could be prepared by dropping acetyl chloride into a highly hindered Grignard reagent especially when ethylmagnesium bromide also was present. When Smith and Guss[1] prepared acetopentamethylbenzene from the hydrocarbon by the Friedel–Crafts synthesis and found the substance to melt at 84°, it was obvious that Clément's compound which melted at 110° could not be acetopentamethylbenzene.

At first it was supposed that Clément's compound was the triketone I, formed from pentamethylphenylmagnesium bromide and acetyl chloride by a sequence of reactions which included: (a) formation of acetopentamethylbenzene, a slow reaction; (b) enolization of the ketone by excess Grignard reagent, a more rapid reaction; and (c) reaction of the enolate with acetyl chloride to give the triketone, also a reaction faster than (a). Accordingly acetopentamethylbenzene was con-



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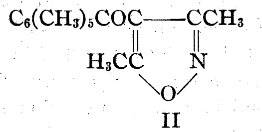

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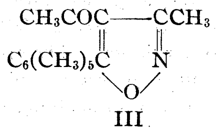

III

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(1) Polymethylbenzenes. XVII. Paper XVI. Smith and Guss, THIS JOURNAL, **59**, 804 (1937).

(2) Henri Clément, *Compt. rend.*, **202**, 425 (1936).

(3) (a) Grignard, *ibid.*, **198**, 625 (1934); (b) Clément and Grignard, *ibid.*, **198**, 665 (1934); (c) Grignard, *ibid.*, **198**, 2217 (1934); (d) see also Urion, *ibid.*, **198**, 1244 (1934).

(4) Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932).

verted to the bromomagnesium enolate by methylmagnesium iodide and by ethylmagnesium bromide, and when the enolate was subjected to the action of acetyl chloride, there resulted a white crystalline substance having the composition $C_{17}H_{22}O_3$ (I), which melted at 110° and which formed a dusty blue, insoluble copper compound from which it could be regenerated by the action of acids. Clément[3b] stated that he had prepared the oxime (m. p. 190.6°) and the semicarbazone (m. p. 241.7°) of his acetopentamethylbenzene. That his "ketone" should form an oxime was in itself an indication that it was not acetopentamethylbenzene, for Baum[5] and also Meyer[6] found that acetomesitylene could not be converted into an oxime by any of the usual methods, although Feith and Davies[7] obtained acetylmesidine, the Beckmann rearrangement product of the oxime, by heating acetomesitylene with hydroxylamine hydrochloride at 160°. Although Clément stated that the analysis of his oxime was in accordance with the theory, he did not publish the figures nor the procedure used, and the logical supposition was that his oxime was the isoxazole II or III, derived from the triketone I. When the triketone I was subjected to the action of hydroxylamine, there resulted the isoxazole II which however, melted at 176° and not at 190.6° as recorded by Clément for his "oxime."

Because the triketone II melted at 110°, the melting point given by Clément for his "acetopentamethylbenzene," the work of Clément was repeated many times before the conviction gradually arose that the agreement between the two melting points was a coincidence and that Clément never had in hand either acetopentamethylbenzene or the triketone. Pentamethylphenylmagnesium bromide was prepared both by the full entrainment method of Grignard, and by the modified method of Kohler and Blanchard.[8] The yield, determined roughly by conversion of an aliquot portion into the acid, was 80 ± 10%. Yet when an ethereal solution of pure acetyl chloride was run into this same Grignard solution, although there was a vigorous reaction, not a trace of acetopentamethylbenzene or of the triketone could be obtained from the reaction product. The product consisted of pentamethylbenzene, bromopentamethylbenzene, and an oily material which, judging from its odor, was largely methyldiethylcarbinol although an appreciable amount of a very high boiling material (b. p. about 180° at 10^{-5} mm.) also was present. Experiments on a known mixture of bromopentamethylbenzene (0.5 g.), pentamethylbenzene (2.0 g.), acetopentamethylbenzene (0.5 g.), triketone (0.39 g.) and ether (25 cc.) showed that 0.12 g. of triketone could be recovered *via* the copper compound, and 0.45 g. of acetopentamethylbenzene could be recovered by treating the remainder of the material with ethylmagnesium bromide, decanting from the insoluble enolate of the ketone, washing the latter thoroughly with ether and then decomposing it with dilute acid.

No product was ever obtained from the reaction between pentamethylphenylmagnesium bromide and acetyl chloride which gave a precipitate when shaken with copper acetate solution; in most cases the yellow or brown ethereal solution merely turned green. And with one exception, no product was ever obtained which gave any enolate of acetopentamethylbenzene when treated with ethylmagnesium bromide. The one exception was the product which resulted when an aliquot portion of a Grignard solution was *added to* excess acetyl chloride. This product (2.5 g.) gave no copper compound, but it did give a crystalline enolate when treated with ethylmagnesium bromide. Decomposition of this enolate gave 0.15 g. (6%) of acetopentamethylbenzene.

Although acetyl chloride, when added to an ethereal solution of pentamethylphenylmagnesium bromide, did not produce either the monoketone or the triketone, nevertheless the Grignard reagent was destroyed by this procedure and the product of the reaction was pentamethylbenzene. This was shown by carbonation of an aliquot portion of the reagent before addition of acetyl chloride, when pentamethylbenzoic acid was obtained; after the reaction with acetyl chloride, carbonation produced no pentamethylbenzoic acid; the only alkali soluble material was a very small amount of a thick orange oil.

The failure to obtain acetopentamethylbenzene from acetyl chloride and the Grignard reagent was surprising in view of the fact that Kohler and Blanchard[8] (p. 370) obtained acetotriphenylbenzene from 2,4,6-triphenyl-phenylmagnesium bromide and acetyl chloride. However, this result was not due to any peculiarity of pentamethylphenylmagnesium bromide, for essentially the

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[5] Baum, *Ber.*, **28**, 3207 (1895).

[6] Meyer, *ibid.*, **29**, 830 (1896).

[7] Feith and Davies, *ibid.*, **24**, 3546 (1891).

[8] Kohler and Blanchard, THIS JOURNAL, **57**, 367 (1935).

same results were obtained when mesitylmagnesium bromide was treated with acetyl chloride. Neither acetomesitylene nor the triketone[4] (p. 4017) derived from it was obtained; the chief product was mesitylene, but along with the hydrocarbon there resulted a small amount of an oily by-product. It appears, therefore, that two methyl groups ortho to the functional group in an aromatic Grignard reagent give rise to a greater hindrance to addition than do two phenyl groups in the same position.

We have not repeated all of Clément's work. He claimed to have obtained (42% yield) acetopentamethylbenzene, also melting at 110°, from the reaction between the Grignard reagent and ethyl acetate. Certainly this is in error. In addition, Clément prepared pentamethylbenzophenone from the Grignard reagent and either benzoyl chloride or ethyl benzoate, and this ketone also gave an "oxime" and a "semicarbazone," a statement which, if true, would indicate that the ketone was not pentamethylbenzophenone. With ethyl formate, Clément obtained *pentamethylbenzaldehyde* in 34% yield, and he reported that the substance melted at 130.5°. Some time ago, Mr. J. H. Paden of this Laboratory prepared this aldehyde from the hydrocarbon, zinc cyanide, hydrochloric acid and aluminum chloride. He found that the aldehyde melted at 142–147° and it was not possible to get a narrower range in the melting point by recrystallizing it, or by distilling it (b. p. 144° at 6 mm.) in an atmosphere of carbon dioxide, followed by crystallization. Nevertheless the aldehyde was analytically pure; it gave an oxime (m. p. 187–188°) and a semicarbazone (m. p. 270–275°), both of which gave excellent analytical values, and on oxidation the aldehyde readily gave the known pentamethylbenzoic acid (m. p. 209–210°).

Experimental Part[9]

Acetopentamethylbenzene was prepared in 80% yield by the method of Smith and Guss.[1] The ketone boiled at 144–145° under 8 mm. pressure, and after crystallization from methanol, the melting point was 84°.

Anal. Calcd. for $C_{13}H_{18}O$; C, 82.11; H, 9.47. Found: C, 82.09; H, 9.21.

When an ethereal solution of the substance was shaken with saturated aqueous copper acetate, no copper compound was formed, nor was there any color developed in the ethereal layer. When subjected for twenty-four hours to the action of hydroxylamine and alkali in aqueous-alcoholic solution according to the procedure of Kamm[10] the ketone (0.2 g.) was recovered quantitatively. No trace of an oxime could be found in the reaction mixture. As shown by Smith and Guss[1] the ketone was enolized completely by methylmagnesium iodide, one equivalent of methane being liberated.

Diacetylpentamethylbenzoylmethane (I).—Acetopentamethylbenzene (5 g.) in ether (50 cc.) was dropped slowly into a solution of ethylmagnesium bromide (25 cc.) prepared from 0.75 g. of magnesium and 2.5 g. of ethyl bromide. The solution developed a light tan color and the white crystalline enolate precipitated. Acetyl chloride (10 cc. freshly distilled from dimethylaniline) in ether (30 cc.) was added slowly. A copious tan precipitate formed, and the ether solution became yellow. The mixture was refluxed for two hours and then allowed to stand for two days, after which it was decomposed by addition of iced hydrochloric acid. The ether layer was separated, the aqueous layer was extracted thoroughly with ether and the combined ethereal solutions shaken with excess saturated aqueous copper acetate. The ethereal layer became blue, and in a short time a bluish-gray precipitate appeared, which was removed and washed with ether. The dull blue copper compound (2.01 g.) turned brown at 234°, sintered at 242° and melted at 244–247° to a deep reddish-brown liquid. The ethereal layer after removal of the copper compound, contained 3.43 g. of acetopentamethylbenzene (m. p. 76–81°) which was contaminated by a small amount of yellow oil.

The copper compound was suspended in ether and decomposed by shaking it with hydrochloric acid (1:1). There resulted 1.67 g. of the triketone (I) which melted at 95–108°. After repeated recrystallization from methanol (6 cc.) the substance melted at 110–111°.

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.45; H, 8.03. Found: C, 74.66; H, 7.71.

When examined quantitatively in the Grignard machine, the triketone in contrast to the analogous compound of Kohler and Baltzly[4] (p. 4021) liberated 1.9 moles of gas and consumed 1.26 moles of reagent by addition (average of two closely agreeing determinations).[11] A few milligrams of the triketone in ether was shaken with copper acetate. After removal of the copper compound, the colorless ether layer was evaporated. Only a trace of material remained.

Isoxazole, II or III.—Two formulas are possible for this substance. It could be 3,5-dimethyl-4-pentamethylbenzoylisoxazole (II) or 3-methyl-4-acetyl-5-pentamethylphenylisoxazole (III), depending upon which carbonyl group enolized after addition of hydroxylamine. The exact structure was not determined. The triketone (0.2 g.) was added to a mixture of hydroxylamine hydrochloride (0.5 g.) in water (2 cc.) and sodium hydroxide (2 cc., 10%). A little alcohol was added to dissolve the triketone, and the mixture was heated on the steam-bath for forty-five minutes. Dilution with water precipitated the isoxazole, which was removed and crystallized from methanol. The melting point was 176°.

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[9] Micro analyses by J. W. Opie.

[10] Kamm, "Qualitative Organic Analysis," John Wiley & Sons, Inc., New York, 1932, p. 172.

[11] The authors are indebted to Mr. Wm. Prichard for the Grignard analyses.

Anal. Calcd. for $C_{17}H_{21}O_2N$: C, 75.28; H, 7.75. Found: C, 75.62; H, 7.85.

Before starting the work on the reactions of pentamethylphenylmagnesium bromide, a control experiment was carried out in order to test the efficiency of the method of analysis which it was proposed to use in handling the products. A mixture (total weight 3.09 g.) of triketone (0.39 g., 0.00146 mole), acetopentamethylbenzene (0.50 g., 0.00338 mole), bromopentamethylbenzene (0.50 g., 0.00186 mole) and pentamethylbenzene (2.00 g., 0.0135 mole) was dissolved in ether (25 cc.) and shaken with copper acetate. There resulted 0.18 g. of copper compound from which 0.12 g. of triketone was obtained. The remaining ethereal solution was shaken with hydrochloric acid, washed with water, and dried. Evaporation of the ether left 2.23 g. of solid material. This was taken up in dry ether (50 cc.) and the solution was added to excess ethereal ethylmagnesium bromide. A white precipitate slowly formed. Stirring and refluxing were continued for six hours and then the mixture was allowed to stand for thirty-six hours at room temperature. The ethereal solution was removed by decantation, the precipitate was washed with a little ether and decomposed in the usual way. There resulted 0.45 g. of crude acetopentamethylbenzene which melted at 64–78°; when mixed with acetopentamethylbenzene, the melting point was 68–78°. The combined ethereal solutions were evaporated; the residue weighed 1.23 g.

The Grignard Reactions.—To a mixture of bromopentamethylbenzene (20 g., 0.088 mole), ether (70 cc.) and magnesium (5.26 g., 0.22 mole) was added dropwise a solution of ethyl bromide (9.62 g., 0.088 mole) in ether (30 cc.). The reaction started at once and the bromopentamethylbenzene began to dissolve. When about half of the ethyl bromide had been added, the Grignard reagent began to precipitate as a white crystalline solid. After all the ethyl bromide was added, the mixture was stirred and refluxed for about an hour. The volume was then made up to 150 cc. by addition of ether and while stirring vigorously 25 cc. was drawn out with a pipet and immediately run onto crushed dry ice in an open beaker. After all the dry ice had disappeared, the mixture was worked up in the usual way. The portion soluble in alkali yielded 1.49 g. (53%) of pentamethylbenzoic acid melting at 202–206°, which when mixed with an authentic specimen (m. p. 209–210°) melted at 205–209°. The alkali insoluble material weighed 0.83 g. and was largely pentamethylbenzene. It melted at 50–58° and the melting point was not changed by addition of pure pentamethylbenzene. Based upon the weights of pentamethylbenzoic acid and pentamethylbenzene (80% pure) obtained, and assuming that both these substances were derived from the Grignard reagent, then the yield of the latter was 80%.

A second 25 cc. of the Grignard solution was pipetted out and dropped slowly into a well-stirred solution of acetyl chloride (10 cc.) in ether (25 cc.). There was a vigorous reaction, a yellow color developed and a precipitate formed. After addition of the Grignard solution the mixture was refluxed for one and one-half hours and then set aside at room temperature for two days. The product was decomposed in the usual way and the combined ethereal solution and extracts when evaporated, gave 2.5 g. of a granular solid which melted at 55–77°. The solid was dissolved in ether and shaken with copper acetate; no copper compound precipitated. The ethereal solution (30 cc.) was dried thoroughly and added slowly to an excess of ethylmagnesium bromide in ether (50 cc.). The mixture was stirred and refluxed for several hours and then set aside overnight. The ether was decanted from the small amount of crystalline precipitate (needles), the latter was washed with ether and then decomposed with acid. There resulted 0.15 g. (6%) of acetopentamethylbenzene which melted at 78–81° and which did not depress the melting point of a known specimen. The ethereal solution and washings, when evaporated, gave 1.19 g. of impure pentamethylbenzene which melted at 50–67°.

Several experiments were carried out in which acetyl chloride in ether was added to the mixed Grignard reagents prepared by the entrainment method. The reaction mixtures were decomposed in the usual way, and the products were worked up as follows.

I. (From 13.3 g. of bromo compound.) The ethereal solution gave no precipitate when it was shaken with copper acetate. The ether was then evaporated and the residue was vacuum distilled. The products were: (a) a colorless oil (1.5 g.) with a sharp odor, which boiled at 33–34.5 under 23 mm., and was probably the chloride of diethylmethylcarbinol; (b) a white solid (6.0 g.) which boiled at 107–114° under 14 mm., and melted at 47.5–51.5° (pentamethylbenzene); (c) a residue of dark viscous liquid in the distilling flask. This was distilled in a high vacuum apparatus. The first material to collect in the receiver was a white solid (0.23 g.) which melted at 95–110° and which gave no copper compound. It was impure bromopentamethylbenzene. When the residue remaining in the distilling flask was heated to 180° under 10^{-5} mm. it gave a distillate (1.39 g.) of light orange oil which darkened immediately on exposure to the air. The non-volatile residue weighed 1.16 g.

II. (From 20 g. of bromo compound.) Before decomposition 50 cc. of the material (total volume 186 cc.) was pipetted out and run into a sufficient excess of ethylmagnesium bromide to destroy the acetyl chloride and enolize any acetopentamethylbenzene that might have been present. Acetyl chloride was then added and the mixture was allowed to stand overnight. Decomposition in the usual way resulted in a dark brown liquid which gave no copper compound. The substance was then steam distilled. The distillate contained pentamethylbenzene (2.97 g.) which melted at 52–55°. The residue remaining in the distilling flask was 1.8 g. of dark oil.

The remainder of the material (136 cc.) after decomposition was first tested with copper acetate (negative) and then steam distilled. From the distillate there was isolated 8.92 g. of pentamethylbenzene which melted at 53–55.5°. The residue consisted of a thick brown oil (3.57 g.).

The total recovery of pentamethylbenzene (11.89 g.) was 91% based on 20 g. of bromo compound used.

III. A Grignard reagent was prepared by refluxing together a dilute ethereal solution of ethylmagnesium bromide (5 cc.), magnesium (2.1 g.), bromopentamethylbenzene (10 g.) and xylene (30 cc.). After refluxing for five hours, excess acetyl chloride was added and refluxing was continued for another hour. The reaction mixture, decomposed in the usual way, gave a negative test with copper acetate, and after drying, gave only a trace of precipitate with excess ethylmagnesium bromide. Acid was added and the mixture was steam distilled. The distillate contained 4.38 g. (68%) of pentamethylbenzene which melted at 54–55° and in the distilling flask there remained 1.79 g. of a thick yellow oil.

IV. A Grignard reagent was prepared by refluxing together the bromo compound (10 g.), magnesium (1.46 g.), ether (100 cc.) and ethyl bromide (1 cc.). The reaction was very slow, but a considerable amount of the Grignard reagent had precipitated after three hours. One-fourth (25 cc.) of the solution was removed and this, dropped onto crushed dry ice and worked up in the usual way yielded 0.65 g. (34.5%) of pentamethylbenzoic acid and 1.12 g. of a mixture of bromo compound and pentamethylbenzene which melted at 77–123°. To the remainder of the Grignard reagent was added acetyl chloride (10 cc.). The mixture was refluxed for two hours and then excess crushed dry ice was added. After carbonation there was obtained as alkali soluble material only 0.3 g. of a yellow malodorous oil which, however, gave a deep green color when it was dissolved in ether and shaken with copper acetate. The alkali insoluble material (5.81 g.) was steam distilled. The distillate contained 3.17 g. of pentamethylbenzene which melted at 51–55° and the residue contained 1.59 g. of yellowish impure bromopentamethylbenzene which melted at 130–140°. Thus, although the Grignard reagent was not converted into acetopentamethylbenzene or the triketone by acetyl chloride, nevertheless it was destroyed by this reagent and in the process it was converted into pentamethylbenzene.

V. An experiment similar to IV was carried out starting with bromomesitylene (10 g.), magnesium (1.3 g.), ether (30 cc.) and ethyl bromide (8 drops). Carbonation of an aliquot portion gave the known carboxymesitylene which melted at 146–150° and which showed no depression in melting point when mixed with an authentic specimen. The remainder of the Grignard solution was refluxed for three hours with acetyl chloride (6 cc.). After decomposition in the usual way, a distillate of 2.98 g. of mesitylene (b. p. 53° under 23 mm.) was removed. The residue (3.59 g.) was taken up in ether and added slowly to excess ethylmagnesium bromide.[4] No precipitate of the enolate of acetomesitylene was obtained after the mixture had stood overnight, nor was any obtained when half the ether was evaporated. The mixture was decomposed and steam distilled, giving a distillate containing 1.2 g. of bromomesitylene and a residue of dark, thick oil (0.89 g.). Hence the Grignard reagent from bromomesitylene behaved toward acetyl chloride in the same manner as the reagent from bromopentamethylbenzene.

Summary

1. Contrary to the report of Clément, pentamethylphenylmagnesium bromide does not give acetopentamethylbenzene when it reacts with acetyl chloride. The products of the reaction are pentamethylbenzene and condensation products of the acid chloride.

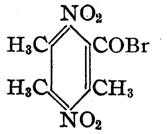
2. Mesitylmagnesium bromide behaves toward acetyl chloride in the same manner as does the reagent from bromopentamethylbenzene, no acetomesitylene resulting. The behavior of the two methylated Grignard reagents differs from that of 2,4,6-triphenyl-phenylmagnesium bromide, which Kohler and Baltzly found gave the aceto compound with acetyl chloride, and these results indicate that two methyl groups in the ortho position to the functional group of a Grignard reagent offer more hindrance to addition than do two phenyl groups similarly placed.

MINNEAPOLIS, MINN. RECEIVED MARCH 15, 1937

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

Polymethylbenzenes. XVIII. The Action of Nitric Acid upon Bromodurene[1]

BY LEE IRVIN SMITH, F. LOWELL TAYLOR AND ISABELLA M. WEBSTER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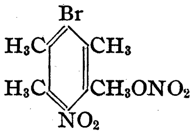
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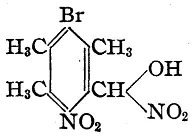
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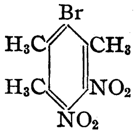
IV

In a recent paper, Smith and Tenenbaum[2] have shown that the product obtained by Willstätter and Kubli[3] by action of fuming nitric acid upon bromodurene, and regarded by them as dinitrodurylic acid bromide (I), could not possibly be an acid bromide. Moreover, the analyses of Smith and Tenenbaum, as well as those of Willstätter and Kubli, agreed much better with the formula $C_{10}H_{11}O_5N_2Br$ than with the formula $C_{10}H_9O_5N_2Br$ (I). The chief reactions of the substance which was discovered by Smith and Tenenbaum were the ready conversion to 3-bromo-5,6-dinitropseu-

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(1) Paper XVII. THIS JOURNAL, **59**, 1078 (1937).

(2) Smith and Tenenbaum, *ibid.*, **57**, 1293 (1935).

(3) Willstätter and Kubli, *Ber.*, **42**, 4151 (1909).

documene (IV) by action of cold concentrated sulfuric acid, and reduction to aminodurene (V). On the basis of these reactions, Smith and Tenenbaum, assuming that the skeleton of bromonitrodurene was still intact in the substance, suggested provisionally that the substance might possess structure II or III. Further work has shown that II, a benzyl nitrate, is the most probable structure for this substance.

The formation of IV ($C_9H_9O_4N_2Br$) from the W.–K. compound ($C_{10}H_{11}O_5N_2Br$) must proceed by elimination of the elements CH_2O. Close observation of the reaction resulted in the detection of the odor of formaldehyde. It was not possible to obtain enough formaldehyde from the reaction to prepare a derivative, due, no doubt, to the destructive action of sulfuric acid upon formaldehyde. A color test with guaiacol carbonate was apparently positive, but was rather indefinite because of the interfering colors.

The W.–K. compound, warmed in acetic anhydride with a little sulfuric acid, gave a substance (VI) having the composition $C_{12}H_{14}O_4NBr$. This substance was the acetate of a bromonitropseudocumyl alcohol, for it was obtained also by acetylation of the substance $C_{10}H_{12}O_3NBr$ (VII) which resulted *along with nitric* acid when the W.–K. compound in 50% acetic acid was refluxed with dilute (0.1 *N*) sulfuric acid. Only traces of nitrous acid were produced in this reaction. The acetate (VI) was hydrolyzed to the alcohol (VII) by the action of alcoholic hydrochloric acid.

When the W.–K. compound was dissolved in absolute ethanol and subjected to the action of sodium ethoxide; there resulted sodium *nitrite* and an orange-yellow solid having the composition $C_{10}H_{10}O_3NBr$ (VIII) which was an aldehyde. A solution of the aldehyde in acetone when treated with alkali, turned green, then blue, and finally a purple substance precipitated. Because of this color reaction, VIII was considered to be an ortho nitro aldehyde. A synthesis of the *o*-nitro-*m*-bromo aldehyde VIII was attempted, but although 6-nitropseudocumyl aldehyde was readily prepared, it could not be brominated, and the action of bromine on durylic aldehyde apparently converted it to a polybromopolymethylbenzyl benzoate.

Since the action of sulfuric acid converts the W.–K. compound into IV, the skeleton D must be intact. Further since reduction gives rise to aminodurene, the fourth side chain carbon must be in place (E). Starting with E($C_{10}H_9O_2Br$) the elements of water and nitrogen dioxide must be added to make up the composition $C_{10}H_{11}O_5N_2Br$ of the W.–K. compound. While the fourth methyl group has been oxidized, it must be in a state such that it can be reduced to methyl again. Both II and III would account for the reduction to aminodurene, but in addition to these two formulas, structures A, B, and C were considered. The chief objection to formulas II and III was the fact that the W.–K. compound gave different products when hydrolyzed in acid and basic media, respectively. Formula C was eliminated entirely on two counts: it would require migration of a methyl group to form IV, and it would lead to an ortho bromo aldehyde for VIII whereas VIII is quite definitely an ortho nitro aldehyde. Formula B also was discarded because it would require a rearrangement with migration of a nitro group to produce IV. Formula A with the trimethylene oxide ring can account for all of the known reactions of the W.–K. compound without the necessity of recourse to any rearrangements, and at first this formula was selected as best representing the chemical behavior of the W.–K. compound. However, Nef[4] and especially Klason and Carlson[5] have shown that the alkaline hydrolysis of benzyl and other nitrates leads to aldehydes and nitrite[6] and that the intermediate compounds are probably peroxides.

$$RCH_2NO_3 + KOH \longrightarrow RCH_2OOH + KNO_2$$
$$RCH_2OOH \longrightarrow RCHO + H_2O$$

With these facts in view, the chief objection to structure II was eliminated and it became necessary to consider this formula as very likely correct. To decide this point, the alcohol VII was converted to the nitrate *via* the chloride IX, and the iodide X. The nitrate so prepared was identical in all respects with the W.–K. compound. While this proof of the structure of the W.–K. compound is not wholly explicit because the intermediates were themselves derived from the W.–K. compound, yet the synthesis, combined with the reversibility of many of the transformations, constitute good implicit proof. Curiously enough, the alcohol VII cannot be converted to the chloride IX by boiling it for an hour with alcoholic hydrochloric acid, a procedure which con-

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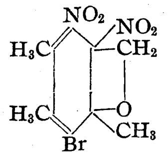
[4] Nef, *Ann.*, **309**, 171 (1899).

[5] (a) Klason and Carlson, *Ber.*, **39**, 2752 (1906); (b) *ibid.*, **40**, 4183 (1907); (c) *ibid.*, **40**, 4191 (1907).

[6] This work was called to the attention of the Authors by the Referee.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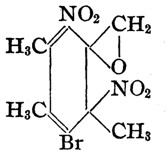
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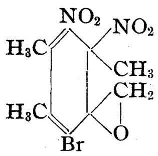
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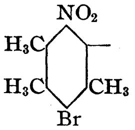
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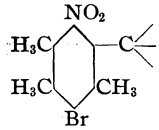
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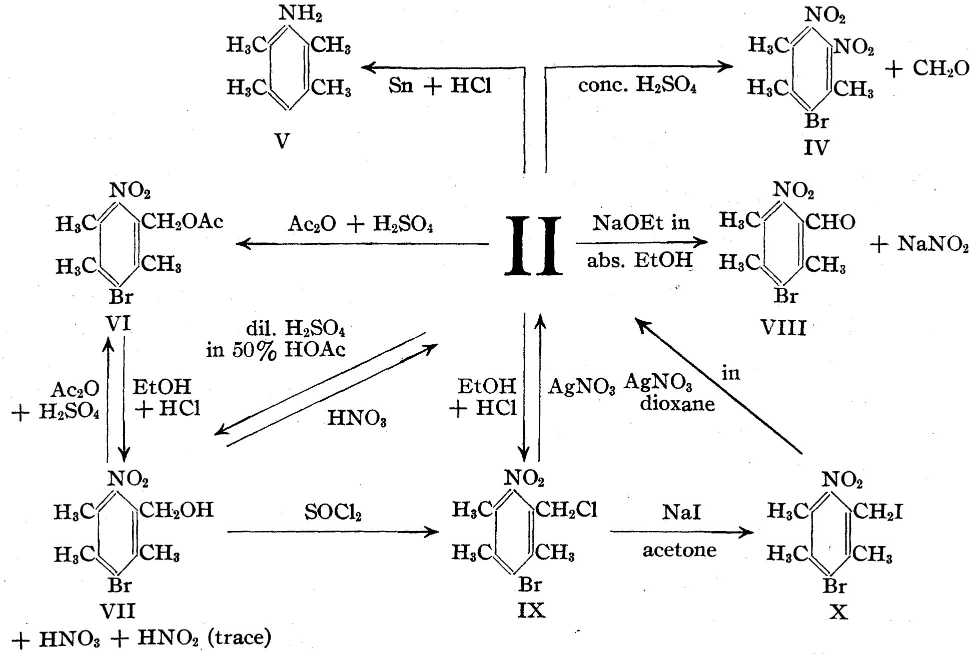

verts the W.-K. compound almost quantitatively to the chloride. These facts indicate that the alcohol is not an intermediate in the latter transformation. Moreover, once the chloride is formed, it is not readily hydrolyzed to the alcohol although the acetate can be converted into the alcohol with ease.

The formation of compounds analogous to the W.-K. compound derived from bromodurene appears to be a general reaction of the highly methylated benzenes and their derivatives. Further work, now in progress, indicates that pentamethylbenzene, dibromodurene, dinitrodurene and possibly some other substances all behave toward cold fuming nitric acid in the same manner that bromodurene does.

While the present work establishes definitely the analogy between the W.-K. compound and Nef's benzyl nitrate, the questions as to whether these compounds are actually nitrates, and if so, the mechanism of their hydrolyses in acid and basic solutions, remain unsettled. Klason and Carlson[5] believed that the nitrates were best represented as derivatives of a per-acid HOONO, but this hypothesis merely shifts the scope of the problem from a peculiar basic hydrolysis to a peculiar acid hydrolysis. It may be that a relationship exists among the forms represented by II, III, and A. The exact relationship, if any, is a problem for future work and it is the present opinion of the authors that while II probably best represents the structure for the W.-K. compound, structure A is not yet definitely excluded.

This work was made possible by a grant from the Fluid Research Fund of the Graduate School of the University of Minnesota.

Experimental Part

Action of Concentrated Sulfuric Acid upon the W.-K. Compound.—As shown by Smith and Tenenbaum, the product of this reaction was IV, and the experiments described below were directed toward detection of formaldehyde. Guaiacol carbonate was dissolved in 90% alcohol and the solution was treated with a little ferric chloride. The W.–K. compound was suspended in sulfuric acid (yellow to orange color) and the solution of guaiacol carbonate was added carefully. At the junction of the two solutions a pink to red ring formed (positive test).

Although it was not likely that formaldehyde could be removed from the sulfuric acid in quantity sufficient for the preparation of a derivative, since sulfuric acid polymerizes and dehydrates it, several attempts were made to isolate the aldehyde. The W.–K. compound (0.5 g.) was placed in a small flask with sulfuric acid (5 cc.). The mixture was warmed while a current of air was passed through it (forty-five minutes) and then bubbled through cold water. The water solution gave no precipitate with dimedon. In a similar experiment, the vapors from the decomposition of the W.–K. compound were passed through a liquid air trap. The condensate in the trap was white when cold, but when warmed to room temperature it became red and had a strong odor of oxides of nitrogen. Nevertheless the water solution was neutralized with bicarbonate and treated with dimedon. No precipitate was obtained.

The W.–K. compound (1 g.) was dissolved in dry ether (50 cc.), sulfuric acid (10 cc.) was added and the ether was slowly distilled through a condenser and an adapter dipping below the surface of cold water. As the ether distilled, fresh ether was added and the distillation was continued until 200 cc. of ether had distilled in four hours. The (neutral) water layer was separated, and the ether was extracted once with water. Dimedon (1.1 g.) in alcohol was added to the combined aqueous solutions, the mixture was warmed and allowed to stand overnight. No derivative of formaldehyde resulted.[7]

2,4,5-Trimethyl-3-bromo-6-nitro-benzyl Alcohol (VII).—The W.–K. compound (3 g.) was dissolved in acetic acid (50 cc.) at room temperature. Water (50 cc.) and sulfuric acid (2 *N*, 5 cc.) were added (precipitation) and the mixture was refluxed in an apparatus which was connected to a wash bottle containing aqueous potassium hydroxide (130 cc., 2%). There was no noticeable evolution of gas, and after refluxing for fourteen to fifteen hours, air was drawn through the apparatus in order to sweep out any oxides of nitrogen. Water was then added and the precipitate (1.8 g.) was removed. The filtrate gave a positive test for nitrate ion with ferrous sulfate and sulfuric acid; a test for nitrite ion was negative, and the solution in the wash bottle when acidified with acetic acid and warmed with Griess' reagent (sulfanilic acid and α-naphthylamine in dilute acetic acid) developed only a faint red color. No more than traces of nitrite were present. The precipitate (m. p. 100–150°) was refluxed with ethanol (25 cc.) and hydrochloric acid (10 cc.) for fifteen minutes. The hot solution was filtered and the filtrate was cooled. The product was removed, washed, and crystallized first from alcohol (20 cc.) and then from benzene (12 cc.)–petroleum ether (5 cc.). The substance was white and melted at 188°.

Anal. Calcd. for $C_{10}H_{12}O_3NBr$: C, 43.78; H, 4.41. Found: C, 43.75, 43.50, 43.95, 43.88; H, 4.38, 4.54, 4.41, 4.38.

When the alcohol (0.38 g.) was dropped into fuming nitric acid (10 cc., d. 1.5) at 0°, a red solution resulted which gradually became lighter and a white solid separated. The product (0.43 g., 97%) was the W.–K. compound, m. p. and mixed m. p. 118–122°.

Acetate (VI).—The alcohol was treated with acetic anhydride and a drop of sulfuric acid; dilution of the mixture precipitated the acetate. Crystallized from ethanol it melted at 85°.

The W.–K. compound (3 g.) was covered with acetic anhydride (20 cc.). Sulfuric acid (6 drops) was added and the mixture was warmed gently (not above 40°) for three days. The mixture when poured into ice water precipitated unchanged material. This was removed and while still damp was treated with the same quantities of reagents. There was a vigorous reaction. The mixture was heated at 70° for twenty-one hours. The product, isolated as before, was crystallized first from ethanol (10 cc.) and then from petroleum ether (12 cc.). It weighed 1.35 g. and melted at 86°. There was no depression in the melting point when the substance was mixed with the acetate prepared from the alcohol.

Anal. Calcd. for $C_{12}H_{14}O_4NBr$: C, 45.57; H, 4.46. Found: C, 45.14, 45.41, 45.02; H, 4.10, 4.50, 4.05.

When the acetate (0.21 g.) was refluxed for fifteen minutes with alcohol (6 cc.) and hydrochloric acid (2 cc.), the product was the alcohol VII, m. p. and mixed m. p., 185–190°.

Chloride (IX).—The W.–K. compound (1 g.) was refluxed with alcohol (40 cc.) and hydrochloric acid (20 cc.) for an hour. The clear yellow solution, when cooled, deposited 1.01 g. of white needles which melted at 110–112°. After crystallization from ethanol or dilute acetic acid, the substance melted at 112.5–113.5°. The chloride (0.85 g.) was also formed when the W.–K. compound (2 g.) was refluxed for sixteen hours with acetone (50 cc.), water (10 cc.) and hydrochloric acid (10 cc.), although the product, when prepared this way, was quite impure.[8]

Anal. Calcd. for $C_{10}H_{11}O_2NBrCl$: C, 41.03; H, 3.79. Found: C, 41.55, 41.85, 41.72; H, 4.23, 4.03, 3.78.

The alcohol (VII) was refluxed with alcoholic hydrochloric acid for one hour and the reaction mixture then allowed to stand overnight. The product was unchanged alcohol. Since this procedure converts the W.–K. compound smoothly into the chloride, the alcohol cannot be an intermediate.

The alcohol (VII) (1 g.) was added to thionyl chloride (5 cc.). A clear solution resulted. The mixture was warmed for five minutes, the excess thionyl chloride was removed under reduced pressure and the yellow residue was crystallized from dilute acetic acid. The substance melted at 107–110° and the melting point was not depressed by mixture with a specimen of the chloride prepared directly from the W.–K. compound.

Hydrolysis of the chloride (0.57 g.) by boiling it with alcohol (50 cc.), water (10 cc.) and potassium carbonate (2 g.) yielded 0.44 g. of product which was essentially unchanged chloride, although the melting point was lowered about 15°.

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[7] Klein and Linser, *Mikrochemie*, Pregl Festschr., 204 (1929).

[8] The preparation of the chloride by both methods was first carried out by J. A. Anthes.

Iodide (X).—The chloride IX (0.86 g.) was added to a solution of sodium iodide in acetone (30 cc., 10%). The reaction was practically instantaneous; sodium chloride was precipitated at once. The mixture was warmed gently for two or three minutes and then allowed to stand for half an hour. The precipitate of crude sodium chloride was removed (weight 0.19 g., theoretical, 0.17 g.) and the filtrate was poured into water. The product weighed 0.97 g. (86%) and melted at 111–113°. Addition of the chloride (m. p. 112–113°) depressed the melting point to 91–96°. After two crystallizations from acetone, the substance formed long white needles which melted at 113–115°.

Anal. Calcd. for $C_{10}H_{11}O_2NBrI$: C, 31.26; H, 2.89. Found: C, 31.30, 31.38; H, 3.33, 3.19.

Nitrate (II) (The W.-K. Compound).—Although the chloride (IX) readily reacted with silver nitrate in ether or in alcohol, precipitating nearly the theoretical amount of silver chloride, the organic product was a mixture from which no pure material could be separated. The reaction was apparently complicated by hydrolysis, for the impure material, even the oily residues obtained by evaporating the mother liquors after crystallization, gave the W.-K. compound when they were dropped into fuming nitric acid.

The iodide, however, could be converted smoothly to the nitrate. The iodide (0.65 g.) and silver nitrate (1 g.) were refluxed in dry dioxane (20 cc.) for two hours, and then kept at 100° for seventeen hours longer. The inorganic material was removed and the dioxane solution was poured into water. The precipitated solid (0.43 g.) was removed and crystallized from alcohol. The melting point, 121–122.5°, was not depressed by addition of the W.-K. compound.

2,4,5 - Trimethyl - 3 - bromo - 6 - nitrobenzaldehyde (VIII).—The W.-K. compound (3 g.) was added to absolute ethanol (25 cc.). The mixture was heated to boiling and to it was added dropwise 2–3 cc. of a solution prepared from sodium (0.3 g.) and absolute ethanol (50 cc.). The color became orange yellow and all the solid dissolved. When cooled, unchanged material precipitated. The mixture was heated again and the alkali added, 1–2 cc. at a time until the transient greenish-yellow color became permanent (30 cc. of the alkali, thirty minutes total time). A precipitate of sodium nitrite separated out. The cooled solution was poured into dilute acetic acid and the solid was filtered off. The filtrate was examined for nitrite ion (positive). The product, crystallized first from ethanol (20 cc.)–benzene (10 cc.) and then from petroleum ether, formed faintly orange needles melting at 193°.

Anal. Calcd. for $C_{10}H_{10}O_3NBr$: C, 44.12; H, 3.71. Found: C, 43.89, 44.09; H, 3.81, 3.67.

The aldehyde could be sublimed. It was sensitive to light, which caused a greenish coloration. A small portion in aqueous acetone was warmed with potassium hydroxide. The solution turned green, then blue, and finally a purple solid precipitated. The same color changes were observed when the W.-K. compound was subjected to the action of alcoholic alkali.

Action of Oxidizing Agents upon the W.-K. Compound.—The substance was rather stable toward oxidizing agents, although it was attacked slowly. After refluxing it with permanganate in 50% acetic acid and sulfuric acid (0.5 cc., 2 *N*) for one and one-half hours, the only isolable product was unchanged material (0.1 g. from 0.3 g.). A similar treatment with sodium dichromate (0.4 g.) in acetic acid (10 cc.) also gave unchanged material (0.28 g. from 0.32 g.).

Bromination of Durylic Aldehyde.—Bromine (6.7 g.) was added to a solution of the aldehyde (6 g.) in cold sulfuric acid (20 cc.) and the mixture was allowed to stand at room temperature for twenty-three hours. The solution was poured into ice water; the small amount of free bromine was removed with bisulfite. The product was removed, extracted with petroleum ether, and the solid residue was crystallized from benzene. It formed colorless needles melting at 219–220° and weighed 1.1 g. It was probably α,2,5-tribromoduryl-2,5-dibromodurylate. It was analyzed but was not examined further.

Anal. Calcd. for $C_{20}H_{19}O_2Br_5$: C, 34.75; H, 2.77. Found: C, 34.32; H, 3.07.

Nitration of Durylic Aldehyde.—The aldehyde (3 g.) and sulfuric acid (10 cc.) were cooled in a freezing mixture (−8°) and nitrated by slow addition (one hour) of a solution of potassium nitrate (2 g.) in sulfuric acid (10 cc.). The cherry red solution after standing for thirty minutes at −15° was poured into ice water. The solid was removed, triturated with bicarbonate, and washed with water. It was dissolved in ethanol (25 cc.), the hot solution was filtered and the filtrate, slowly cooled, deposited 1.6 g. of fine plates melting at 139–140°. The aldehyde could not be brominated.

Summary

1. A further study of the reaction between bromodurene and fuming nitric acid has shown that of the formulas heretofore suggested, II, 2-nitro-5-bromo-3,4,6-trimethylbenzyl nitrate, at present best represents the chemical behavior of the product.

2. The reaction appears to be a general property of the highly alkylated benzenes and certain of their derivatives.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 25, 1937

[CONTRIBUTION FROM THE LABORATORIES OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA AND THE UNIVERSITY OF ILLINOIS]

The Bromination of 4-Phenylphenylbenzenesulfonate

BY STEWART E. HAZLET[1]

Although much work has been done to determine the orienting effect of phenolic hydroxyl groups, only a few studies have been made of the modification of the directive influence of such functional groups by esterification. In the present work a study has been made of the bromination of 4-phenylphenol and one of its esters. It has been found that bromination of 4-phenylphenol (I) yields 2-bromo-4-phenylphenol (II), but when the hydroxyl group is modified to benzenesulfonyloxy the bromination product is 4-(4-bromophenyl)-phenylbenzenesulfonate (V). The reactions and proof of structure of the compounds are summarized in Chart I.

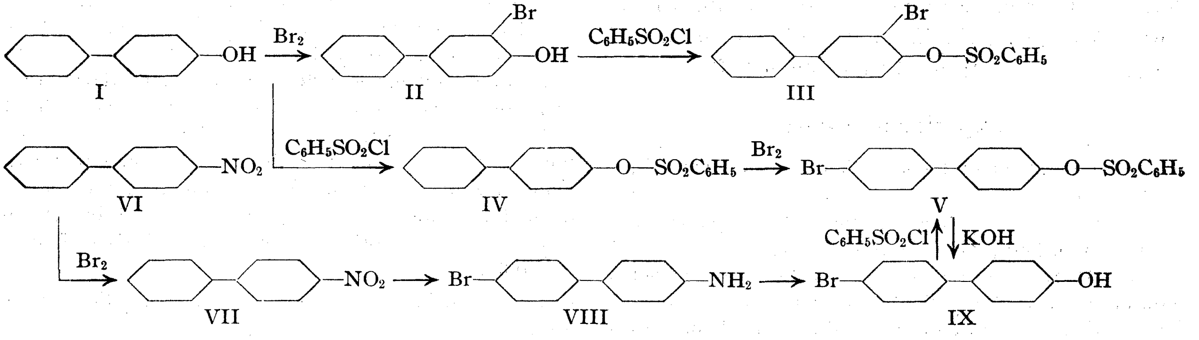

CHART I

There are some other cases on record in which esterification of phenolic groups modified their directive influence. Raiford and Stoesser[2] found that, although bromination of vanillin gives a high yield of the 5-bromo derivative, acetylvanillin, under the same circumstances, gives only the 6-bromo substitution product. Benzoylvanillin was found by Raiford and Milbery[3] to behave in the same manner. It is claimed that halogen takes the position (6) because of the directive influence of the methoxy radical, and that this influence comes into play after the directive power of hydroxyl has been largely suppressed by acylation.

Also it is known that, although halogenation and nitration of 4-phenylphenol[4] follow the normal course, the first substituent entering the position ortho to hydroxyl, when the hydroxyl group is modified to the methoxy group, nitration yields 80% of 2-nitro-4-phenylanisole, and 15% of 4-(4-nitrophenyl)-anisole is obtained as well.[5] When the 4-toluenesulfonyloxy group is present in the molecule rather than the hydroxyl or methoxy, the nitration product is reported[5] as "mainly, if not exclusively" 4-(4-nitrophenyl)-phenyl-4-toluenesulfonate. Apparently the bromination of similar substances has not been studied.

Upon nitration, 4-phenylacetanilide gives 2-nitro-4-phenylacetanilide,[6] and 4′-phenyl-4-toluenesulfonanilide gives 2′-nitro-4′-phenyl-4-toluenesulfonanilide.[5] The bromination of the first of these compounds has been shown to give 50% of 2-bromo-4-phenylacetanilide and 30% of 4-(4-bromophenyl)-acetanilide,[7] and in the case of the sulfonanilide bromination gives a mixture of compounds.[8] Hence, it was desirable to know whether bromination of esters such as IV would parallel nitration. From the results here reported, it is evident that the bromination of IV proceeds as does the nitration of the similar compound.

By the method of mixed melting points, V was shown to be different from III and identical with the benzenesulfonic acid ester of IX. By the same procedure, the phenolic hydrolysis product from V was shown to be IX and not II.

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[1] Present address, Department of Chemistry, State College of Washington, Pullman, Washington.

[2] Raiford and Stoesser, THIS JOURNAL, **49**, 1078 (1927).

[3] Raiford and Milbery, *ibid.*, **56**, 2727 (1934).

[4] Raiford and Colbert, *ibid.*, **47**, 1457 (1925); Colbert and others, *ibid.*, **56**, 202, 2128 (1934).

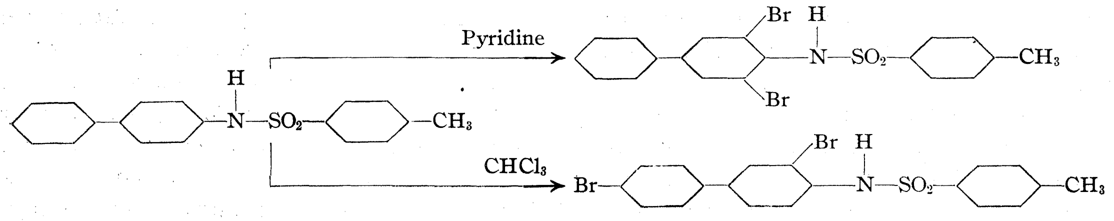
[5] Bell and Kenyon, *J. Chem. Soc.*, **129**, 3046 (1926).

[6] Banus and Tomas, *Anales soc. españ. fís. quím.*, **19**, 293 (1921); Fichter and Schulzberger, *Ber.*, **37**, 878 (1904).

[7] Kenyon and Robinson, *J. Chem. Soc.*, **129**, 3050 (1926).

[8] Bell, *ibid.*, **134**, 2338 (1931).

Since glacial acetic acid was the solvent used in the bromination of IV, whereas chloroform had been used previously in the preparation of II,[7] it was necessary to determine whether the solvent might have caused the difference. Such a difference due to solvent has been observed in the case of the bromination of a sulfonanilide[8]



However, bromination of I in glacial acetic acid under the same conditions which were used for the bromination of the ester (IV) gave the same product (II), in 82.5% yield, as had been obtained using chloroform as solvent. Therefore, the difference in directive influence must be due to the presence of benzenesulfonoxy in place of hydroxyl and cannot be attributed to a solvent effect.

Experimental Part

4 - (4 - Bromophenyl) - phenylbenzenesulfonate (V).—4-Phenylphenylbenzenesulfonate[9] (IV) (20 g.) was suspended in 200 cc. of glacial acetic acid and heated on a boiling water-bath, with vigorous stirring. Bromine (4.5 cc.) was then introduced slowly, and a trace of powdered iron was added. After all of the bromine had been added, the reaction was allowed to proceed for three hours; then the mixture was cooled and poured into five volumes of cold water. After filtering, the reaction product represented a 97% yield. It was recrystallized from alcohol, and a colorless product, m. p. 79–81°, was obtained.

Anal. Calcd. for $C_{18}H_{13}O_3BrS$: Br, 20.57. Found: Br, 20.95.

To prove the structure of the above, it was prepared in the following manner. 4-(4-Bromophenyl)-nitrobenzene (VII) was prepared according to the method of Le Fèvre and Turner.[10] The nitro compound (VII) was reduced to 4-(4-bromophenyl)-aniline (VIII),[10] and this was converted to 4-(4-bromophenyl)-phenol (IX), as directed by Bell and Robinson.[11] The product thus obtained melted between 163 and 165°. When 4-(4-bromophenyl)-phenol (IX), in pyridine solution, was treated with benzenesulfonyl chloride, 4-(4-bromophenyl)-phenylbenzenesulfonate (V), m. p. 78–80°, was obtained. This material was mixed with the brominated ester, and a melting point of 78–80° was observed.

Hydrolysis of 4-(4-Bromophenyl)-phenylbenzenesulfonate.—One gram of the ester (V) was suspended in 100 cc. of a 10% potassium hydroxide solution (alcohol: water:: 1:1), and allowed to reflux for twenty-four hours. The reaction mixture was diluted with an equal volume of water and extracted with ether. The aqueous solution was acidified and the phenolic component extracted with ether. The ethereal solution was dried with anhydrous sodium sulfate to which some Norite had been added. After filtering and removing the solvent by evaporation, an 86% yield of crude 4-(4-bromophenyl)-phenol (IX) was obtained. This was crystallized from alcohol, and the purified material (55% yield) melted at 165–166°. The product prepared in this manner was purified much more easily than that prepared by the method of Bell and Robinson.[11] The mixed melting point of the substances prepared by the two methods was 163–165°.

2-Bromo-4-phenylphenylbenzenesulfonate (III).—Five grams of II was dissolved in pyridine and treated with 1.1 mols. of benzenesulfonyl chloride. The oily product, obtained by extraction with ether in the usual manner,[9] represented an 81% yield. After standing several months, it solidified and was crystallized from slightly diluted methanol. The colorless product (51% yield) melted at 102–103°.

Anal. Calcd. for $C_{18}H_{13}O_3BrS$: S, 8.24. Found: S, 8.18.

2,6 - Dibromo - 4 - phenylphenylbenzenesulfonate.—2,6-Dibromo-4-phenylphenol was prepared by a known method.[11] From 5 g. of this hydroxyl compound, the pure benzenesulfonic acid ester was obtained in 84% yield by the usual method;[9] alcohol was used as solvent for recrystallizations. The colorless product melted between 145 and 147.5°.

Anal. Calcd. for $C_{18}H_{12}O_3Br_2S$: Br, 34.19. Found: Br, 34.44.

Summary

1. Although bromination of 4-phenylphenol in glacial acetic acid solution yields 2-bromo-4-phenylphenol, under the same circumstances bromination of 4-phenylphenylbenzenesulfonate yields 4-(4-bromophenyl)-phenylbenzenesulfonate.

2. Some related compounds have been reported.

3. Further work is in progress.

RECEIVED MARCH 29, 1937

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[9] Hazlet, THIS JOURNAL, **59**, 287 (1937).

[10] Le Fèvre and Turner, *J. Chem. Soc.*, **129**, 2045 (1926).

[11] Bell and Robinson, *ibid.*, **130**, 1127 (1927).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Preparation and Properties of a Series of Alkyl Thiolacetates[1]

BY F. W. WENZEL, JR., AND E. EMMET REID

This is a continuation of the comparison of sulfur compounds with their oxygen analogs.[2] The task undertaken was the preparation of the thiolacetates of the normal alcohols, or rather the acetyl derivatives of the mercaptans, from methyl to octyl, and the determination of their physical properties.

Thiol esters usually have been prepared by the action of an acid chloride on a mercaptan or mercaptide. The esters here described were made from the mercaptans (a) by treating them with acetyl chloride, (b) by refluxing them with acetanhydride and sodium acetate, and (c) by dissolving them in strong caustic soda and adding acetanhydride. Method (c) is preferred for the lower mercaptans which are too volatile for (b) and which dissolve readily in aqueous alkali, while (b) is best for the higher members. The properties of these esters are given in Table I and some are plotted in Figs. 1 and 2 along with the corresponding data for the oxygen esters.

TABLE I

Normal alkyl	B. p., °C. 760 mm.	d^0_4	d^{25}_4	n^{25}_D	Mol. refraction Calcd.	Mol. refraction Found	Sulfur, % Calcd.	Sulfur, % Found	
Methyl	98.0[a]	1.0461	1.0170	1.4600	24.03	24.27	35.58	34.89	35.41
Ethyl	116.4[b]	1.0006	0.9739	1.4540	28.65	29.05	30.79	30.93	30.64
Propyl	139.8[c]	0.9789	.9537	1.4558	33.27	33.65	27.14	26.83	26.80
Butyl	163.4	.9628	.9390	1.4570	37.89	38.33	24.26	24.36	24.22
Amyl	185.1	.9511	.9285	1.4579	42.51	42.94	21.93	21.87	21.77
Hexyl	205.8	.9408	.9192	1.4591	47.13	47.66	20.01	19.92	20.18
Heptyl	227.4	.9334	.9128	1.4600	51.74	52.29	18.40	18.40	18.36
Octyl	247.0	.9259	.9058	1.4609	56.36	57.04	17.03	17.15	17.25

[a] Ralston and Wilkinson, THIS JOURNAL, **50,** 2160 (1928) reported 95–96°.

[b] Hepworth and Clapham, *J. Chem. Soc.*, **119,** 1188 (1921), give 116–117°; Baker and Reid, THIS JOURNAL, **51,** 1567 (1929), found 116–117°, d^0_4 1.0008, d^{25}_4 0.9755, r^{28}_D 1.4503.

[c] According to Ralston and Wilkinson, 135–137°.

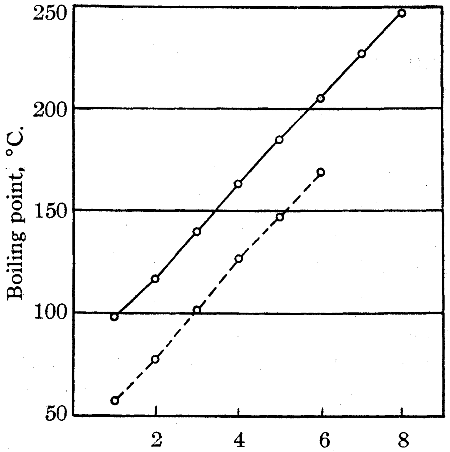

Fig. 1.—Boiling points: normal thiolacetates ————; normal acetates – – – – –.

The amount by which the boiling point of an acetate is raised by the substitution of —S— for —O— is 40° for the methyl and decreases slightly as the series is ascended. Methyl thiolacetate has the same molecular weight as butyl mercaptan and both boil at 98°, but the higher members of the series boil somewhat lower than the mercaptans of the same molecular weight.

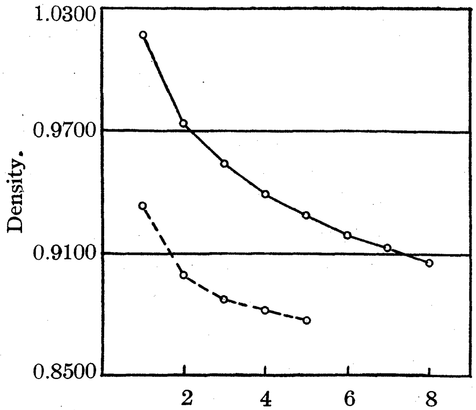

Fig. 2.—Densities: normal thiolacetates at 25° ————; normal acetates at 20° – – – – –.

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[1] Read at the Cincinnati meeting of the American Chemical Society, 1930.

[2] THIS JOURNAL, **37,** 1934 (1915); **38,** 2757 (1916); **39,** 1930 (1917); **54,** 1685 (1932).

Experimental

The higher alcohols, alkyl bromides, and mercaptans were prepared by standard methods and fractionated through precision stills,[3] cuts taken of 1° or less. Ethyl mercaptan was purchased and methyl mercaptan was prepared according to Klason.[4]

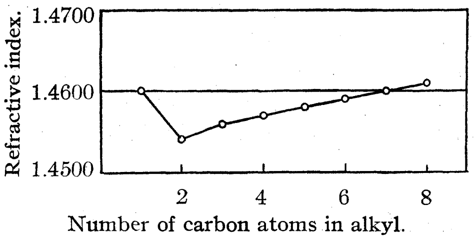

Fig. 3.—Refractive indices of normal thiolacetates.

Preparation of the Esters. Method (a).—To the mercaptan in a flask packed in ice the calculated amount of acetyl chloride was added slowly from a dropping funnel through a reflux condenser. The flask was allowed to come to room temperature at which it was kept for three days and then emptied into water. The ester was washed, dried over calcium chloride, and distilled. Four hundred and ten grams of ethyl thiolacetate, b. p. 115.5–116.5°, was prepared by this method with yields from 60–70%; also 55 g. of *n*-propyl, b. p. 138–140°, yield 70%, and 67 g. of *n*-butyl, b. p. 162–164°, yield 91%.

Method (b).—A mixture of 1 mole of mercaptan and 1.2 moles of acetanhydride and one-fifth of its weight of anhydrous sodium acetate was refluxed for an hour by the use of an oil-bath which was raised from 130° at the start to 150° at the end of this time. The reaction usually became so vigorous, after short heating, that the flask had to be removed from the oil-bath for a time. The cooled mixture was poured into water, the ester separated, washed free of acid, dried, and distilled. Thirty-three grams of ethyl thiolacetate, b. p. 115.5–116.5°, yield 78.5%, was prepared by this method; also 35 g. of *n*-butyl, b. p. 162–164°, yield 95%; 68 g. of *n*-amyl, b. p. 182.5–185°, yield 92.5%; 64 g. of *n*-hexyl, b. p. 204–206°, yield 94%; 108 g. of *n*-heptyl, b. p. 145.5–146° at 70 mm., yield 91%; and 48 g. of *n*-octyl, b. p. 146.5–147° at 38 mm., yield 93%. Seventy grams of the methyl thiolacetate, b. p. 98–99°, was prepared by passing methyl mercaptan directly into the boiling anhydride–sodium acetate mixture.

Method (c).—A mixture of 40 g. of sodium hydroxide, 75 cc. of water, and 1.2 mole of mercaptan was poured over 500 g. of shaved ice in a flask and 1.25 mole of acetanhydride was added rapidly with vigorous stirring which was continued for five minutes. The ester was separated immediately and worked up as in method (b): 100 g. of ethyl thiolacetate, b. p. 115.5–116.5°, yield 79.3%, was prepared by this method.

Conclusion

A series of normal alkyl thiolacetates have been prepared by various methods and their physical properties determined.

BALTIMORE, MD. RECEIVED APRIL 13, 1937

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[3] Ellis and Reid, THIS JOURNAL, **54**, 1685 (1932).

[4] Klason, *Ber.*, **20**, 3049 (1887).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

Some Monothioformals

BY F. W. WENZEL, JR., AND E. EMMET REID

Formals are well known, and a few dithioformals have been prepared, but the intermediate monothioformals, $ROCH_2SR$, have been neglected.[1] The purpose of this investigation was to prepare and study several of these, so as to compare them with the formals and the dithio compounds.

They are obtained readily from a chloromethyl alkyl ether and a mercaptan in alkaline solution

$$RSNa + ClCH_2OR = RSCH_2OR + NaCl$$

They can be made also from lead mercaptides in benzene solution. On account of side reactions the yields are only fair, about 50%. Care must be taken to get rid of any remaining chloromethyl ether, otherwise hydrochloric acid will be generated and the product decomposed.

The compounds chosen for study were the ethyl, *n*-propyl, and *n*-butyl. The data obtained are given in Table I.

The monothioformals are stable; the diethyl compound was refluxed for eight hours without any sensible change. However, if 1% of hydrogen chloride is added, rearrangement takes place and a formal and a dithioformal are obtained, the equilibrium being readjusted as the most volatile constituent is removed. On account of this instability in the presence of acid, care must be taken in the preparation of a monothioformal not to leave any of the chloroether in the crude product.

It is known that a Grignard reagent does not react with formals below 100°.[2] We have found this to be true with a monothioformal. Heating

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[1] Since our work was completed Böhme has made the diethyl derivative. *Ber.*, **69**, 1610 (1936).

[2] Späth, *Monatsh.*, **35**, 319 (1914).

TABLE I

PHYSICAL PROPERTIES AND ANALYSIS OF THE MONOTHIOFORMALS

	B. p., °C. 760 mm.	d^0_4	d^{25}_4	n^{25}_D	Mol. refraction Calcd.	Mol. refraction Found	Sulfur, % Calcd.	Sulfur, % Found	
Diethyl	135.8[3]	0.9363	0.9122	1.4432	34.90	34.94	26.68	26.13	26.20
Di-*n*-propyl	179.2	.9185	.8960	1.4473	44.14	44.23	21.51	21.76	21.11
Di-*n*-butyl	220.0	.9061	.8853	1.4500	53.38	53.51	18.10	18.04	18.27

Ethylal boils 47.8° below and the diethyl methylene mercaptal 48° above the diethyl monothioformal.

the diethyl compound with ethylmagnesium bromide at 100° for five hours decomposed less than one-third of it. Ethyl mercaptan and ethyl propyl ether were identified as the reaction products, which shows that the —SR is replaced more readily than the —OR.

Oxidation of a monothioformal takes place readily, but we have been unable to isolate a sulfone.

Experimental

In the preparation of the monothioformals the mercaptan was dissolved in about five volumes of alcohol and the equivalent amount of sodium hydroxide added. This solution was cooled to 0° and an equivalent of the chloroether added dropwise with stirring. Sodium chloride precipitated at once. The mixture stood overnight and was diluted with an equal volume of water. The top layer was separated, washed with water, dried over potassium carbonate, and fractionated at 100 mm., a 1° cut being taken. There was always a considerable amount of a low boiling fraction, apparently the formal. The boiling points of the best fractions were determined with a Cottrell apparatus with a calibrated thermometer and analysis for sulfur made by a Parr bomb.

A sample of the diethyl monothioformal was refluxed for eight hours and distilled. The boiling point and other properties were unchanged. Into a 90-g. sample (0.75 mole) about 1% of hydrogen chloride was passed. It was refluxed for eight hours, moisture being excluded. Fractionation separated it into two main fractions: (1) 30 g. (0.29 mole) boiling at 85–89° at 760 mm., d^{25}_4 0.8301, n^{25}_D 1.3715; and (2) 48.5 g. (0.36 mole) boiling at 186° and containing 45.87% sulfur, yielded a sulfone, m. p. 103°. Ethylal has b. p. 88° and d^{20}_4 0.8318 and diethyl methylene mercaptal has b. p. 184°, 47.07% sulfur, and gives a sulfone, m. p. 104°.[4]

To 148 g. of the dipropyl monothioformal the Grignard reagent from 137 g. of butyl bromide in ether was added and the mixture refluxed for four hours. By working this up in the usual way 86% of the monothioformal was recovered with unchanged properties and tests for mercaptan were negative. In a second experiment 120 g. of the diethyl derivative was treated with ethylmagnesium bromide, the ether distilled off, and the residue heated to 100° for five hours. The product was worked up as usual and fractionated. The first fraction was ethyl mercaptan, identified by the α-anthraquinone thio ether.[5] The second fraction had b. p. 63.5°, d^{25}_4 0.7360, n^{25}_D 1.3745 which identified it as ethyl *n*-propyl ether, b. p. 61.4, d^{20}_4 0.732, n^{20}_D 1.3695. The third fraction, 71–78° at 100 mm. was the unreacted thioformal and accounted for 70% of that taken.

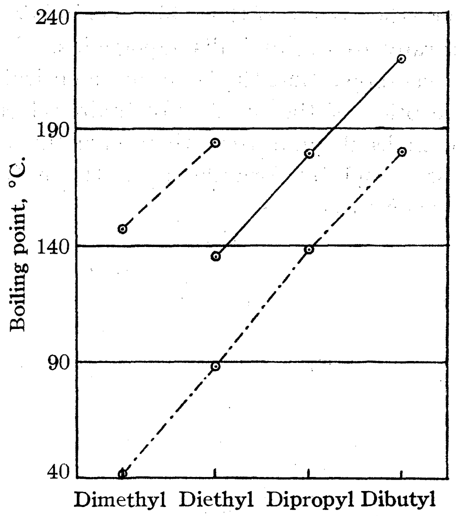

Fig. 1.—Boiling points: monothioformals ————; dithioformals - - - - - -; formals — - — - - - -.

Summary

1. Diethyl, di-*n*-propyl and di-*n*-butyl monothioformals were prepared by treating the sodium mercaptide with the chloromethyl alkyl ether, and their physical properties were determined.

2. A monothioformal, heated with hydrogen chloride, rearranges into a formal and a dithioformal.

3. They react, but not readily, with ethylmagnesium bromide.

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[3] Böhme gives 134–136° at 755 mm.

[4] Claesson, *J. prakt. Chem.*, [2] **15**, 176 (1877).

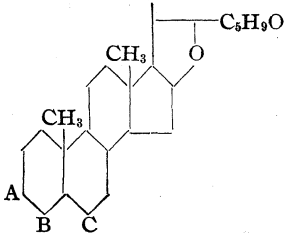
[5] Reid, Mackall and Miller, THIS JOURNAL, **43**, 1199 (1921).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

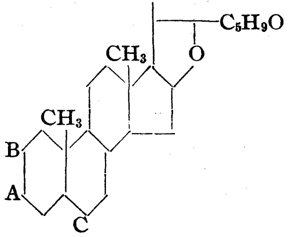
Saponins and Sapogenins. V. Oxidation Products and Structure of Chlorogenin

BY C. R. NOLLER

Chlorogenin, one of the two sapogenins isolated from the hydrolysis products of extracts of *Chlorogalum pomeridianum*[1] has the empirical formula $C_{27}H_{44}O_4$.[2] It is therefore isomeric with gitogenin and like gitogenin contains two hydroxyl groups and two oxygen atoms having non-reactive linkages which are assumed to be oxidic. Since the other sapogenin accompanying chlorogenin is apparently identical with tigogenin, which accompanies gitogenin and digitogenin in the hydrolysis products of extracts of digitalis, it was further assumed that chlorogenin is related structurally to the digitalis sapogenins. Recent work[3] has shown that the latter are identical with the exception of the number of hydroxyl groups in the molecule and that their structures may be represented by formula I or II, preference being given to II.



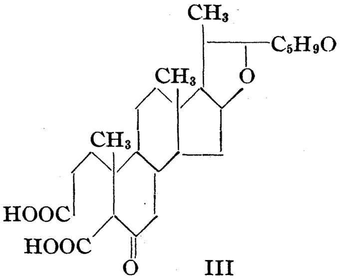
I



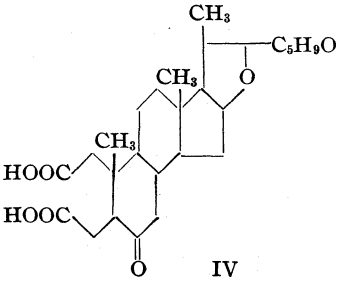
II

Tigogenin has its one hydroxyl group at A, gitogenin's two are at A and B, and digitogenin's three at A, B and C. A third sapogenin of unknown structure but isomeric with gitogenin is also present in the hydrolysis products of digitalis extracts, since Windaus and Shah[4] report the isolation from the oxidation products of crude digitogenin of a diketone, $C_{27}H_{40}O_4$, which is not the diketone corresponding to gitogenin.

It was thought that chlorogenin might have structure I or II with its two hydroxyl groups at A and C. If this were the case one might expect to find digitogenic acid, III or IV, in the oxidation products since opening of ring I might take place on either side of A with simultaneous conversion of the secondary hydroxyl group at C to a carbonyl group.



III



IV

On the other hand, it was conceivable that chlorogenin was identical with the unknown sapogenin of Windaus and Shah, in which case their diketone would be obtained on oxidation.

Oxidation of chlorogenin by the procedure of Kiliani and Merk[5] for the preparation of digitogenic acid showed that neither of these possibilities is actually the case. Both a diketone, $C_{27}H_{40}O_4$, and a ketodibasic acid, $C_{27}H_{40}O_7$, were obtained but they were not identical with the previously reported diketone or with digitogenic acid.

Since a diketone is formed, both hydroxyl groups in chlorogenin must be secondary. The diketone forms a dioxime but only a mono-*o*-phenylenediamine derivative which is not a quinoxaline. This shows that the two ketone groups are not adjacent and indicates that one is

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[1] Liang and Noller, THIS JOURNAL, **57**, 525 (1935).

[2] Fieser and Jacobsen, *ibid.*, **58**, 943 (1936).

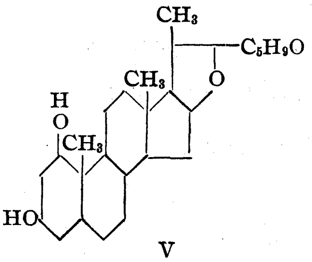
[3] Jacobs and Simpson, *J. Biol. Chem.*, **110**, 429 (1935); Tschesche, *Ber.*, **68**, 1090 (1935); Tschesche and Hagedorn, *ibid.*, **68**, 1412, 2247 (1935); **69**, 797 (1936).

[4] Windaus and Shah, *Z. physiol. Chem.*, **150**, 205 (1925).

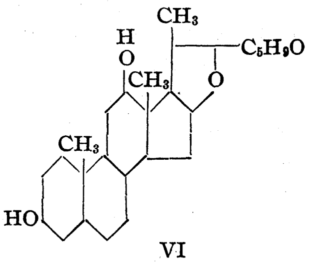
[5] Kiliani and Merk, *Ber.*, **34**, 3564 (1901).

sterically hindered. The pure diketone on further oxidation gives the same ketodibasic acid obtained by the direct oxidation of chlorogenin so that the diketone is probably an intermediate in the formation of the acid. The dibasic acid gives a dimethyl ester which is readily saponified to the original acid indicating that neither carbomethoxy group is sterically hindered. Chlorogenin is not precipitated from alcoholic solutions by digitonin but if the diketone is reduced with sodium and alcohol, a small amount of material is obtained which is slowly precipitated by digitonin.[6] This indicates that one of the hydroxyl groups in chlorogenin is at A but that the configuration is the opposite of that present in cholesterol.[7]

Assuming that the side chain has the same structure as that in the digitalis sapogenins, a consideration of the above data leads to formulas V and VI as being the most likely for chlorogenin. Because of the small amount of the ketodibasic acid that has been available it has not been possible to determine its structure but it does not appear to be either an α- or β-keto acid so that formula VI is favored.



V



VI

Experimental

Oxidation of Chlorogenin.—In a typical run 5 g. of chlorogenin, m. p. 277–279°, was covered with 50 cc. of glacial acetic acid, the flask placed in a pan of water and 40 g. of the sodium dichromate–sulfuric acid oxidizing mixture of Kiliani and Merk[5] added in small portions with shaking during the course of two or three minutes. The chlorogenin goes into solution almost completely and then the product begins to precipitate. After standing overnight the product was filtered, washed with 30% acetic acid until the filtrate was colorless, and then thoroughly with water.

Diketone, $C_{27}H_{40}O_4$.—The moist oxidation product was taken up in 200 cc. of benzene and extracted twice with 5% sodium carbonate solution and once with water. The cloudy benzene solution settled on standing overnight and was decanted. Concentration on the steam-bath to 30 cc., filtering hot and cooling gave 1.7 g., m. p. 233–235°. Evaporation of the mother liquor to dryness gave 1.1 g., m. p. 230–235°. The product is too soluble in benzene or dioxane for good crystallization, but crystallizes well from methyl alcohol, ethyl alcohol and acetone. After repeated recrystallization from all three solvents the fine needles shrink at 236° and melt at 247–248°; $[\alpha]^{22}_{D}$ − 69.6, $[\alpha]^{22}_{546.1}$ −81.4 in dioxane. The diketone appears to be dimorphous as it sometimes melts sharply at 236–238° and the melting point is not raised by further recrystallization.

Anal.[8] Calcd. for $C_{27}H_{40}O_4$: C, 75.67; H, 9.40. Found: C, 75.37; H, 9.45.

Dioxime, $C_{27}H_{42}O_4N_2$.—A mixture of 0.1 g. of diketone and 0.14 g. of crystalline sodim acetate was dissolved in boiling alcohol, and 0.07 g. of hydroxylamine hydrochloride added. After refluxing for four hours, the solution was poured into water, washed and dried in air. After several recrystallizations from absolute ethyl acetate, it melted at 242–243°. An alcoholic solution of the dioxime does not react with solutions of nickel salts.

Anal. Calcd. for $C_{27}H_{42}O_4N_2$: C, 70.72; H, 9.22; N, 6.11. Found: C, 70.70; H, 9.15; N. 5.80.

o-Phenylenediamine Derivative, $C_{33}H_{46}O_3N_2$.—A solution of 0.08 g. of diketone and 0.04 g. of *o*-phenylenediamine in 5 cc. of alcohol was refluxed for one hour. On cooling, tan colored crystals separated which melted at 254–261° with decomposition to a red oil. Repeated crystallization from alcohol gave a pale yellow product which melted at 255–261° when heated slowly but melted at 265–267° when the capillary tube was placed in a bath preheated to 255°.

Anal. Calcd. for $C_{33}H_{44}O_2N_2$: C, 79.16; H, 8.85; N, 5.59. Calcd. for $C_{33}H_{46}O_3N_2$: C, 76.40; H, 8.95; N, 5.40. Found: C, 76.30; H, 8.90; N, 5.26.

Ketodibasic Acid, $C_{27}H_{40}O_7$.—The sodium carbonate extracts of the crude oxidation product were acidified with 15% hydrochloric acid. Only the first extract gave a precipitate, which was filtered, washed and dried in air. There was obtained 0.109 g., m. p. 196–200°. This acid is insoluble in benzene, very soluble in dioxane and soluble in hot acetone, ethyl acetate and chloroform. It does not crystallize well from any of these solvents or their mixtures with benzene. It is very soluble in acetic acid but crystallizes well from hot concentrated solutions. The combined acid fractions from several oxidations after repeated crystallization from acetic acid melted at 235–237° with decomposition and preliminary shrinking; $[\alpha]^{22}_{D}$ − 42.8, $[\alpha]^{22}_{546.1}$ − 49.0 in dioxane. As the analyses show, this product, which was dried by allowing it to stand for several weeks in a vacuum desiccator over potassium hydroxide, contains one molecule of acetic acid of crystallization.

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(6) We are indebted to Mr. F. M. McMillan for this information.

(7) Fernholz, *Z. physiol. Chem.*, **232**, 97 (1935).

(8) All carbon, hydrogen and nitrogen analyses are by Dr. A. Schoeller, Berlin.

Anal. Calcd. for $C_{25}H_{38}O_3(COOH)_2 \cdot CH_3COOH$: C, 64.91; H, 8.26; neut. equiv., 178.7. Found: C, 65.89; H, 8.53; neut. equiv., 176.1.

The solutions from the above determinations of neutralization equivalent were evaporated to a small volume on the steam-bath, diluted to 25 cc. with water, filtered and acidified with 0.05 *N* hydrochloric acid. The precipitate was filtered on a hardened paper and washed with hot water until free of chlorides. After drying it melted at 234–236° and analysis showed it to be free of acetic acid.

Anal. Calcd. for $C_{25}H_{38}O_3(COOH)_2$: C, 68.05; H, 8.46; neut. equiv., 238.3. Found: C, 68.03; H, 8.30; neut. equiv., 240.5.

In order to determine whether this dibasic acid was derived from the diketone, 3.5 g. of pure diketone was covered with 35 cc. of acetic acid and treated with 28 g. of the oxidizing mixture of Kiliani and Merck. After fifty-two hours the product was filtered and washed, and amounted to 0.8 g. The filtrate was diluted to 1 liter and filtered. The light green precipitate was dissolved in 15 cc. of hot glacial acetic acid and poured into 500 cc. of water. The precipitate after drying weighed 0.5 g. The total product of 1.3 g. was dissolved in benzene, extracted with sodium carbonate solution and the extract acidified. After filtering, washing and drying, the acid fraction weighed 0.3 g. and melted at 210–215°. After recrystallization from acetic acid it melted at 235–237° with decomposition and did not depress the melting point of the acid obtained by the direct oxidation of chlorogenin.

Dimethyl Ester of Ketodibasic Acid.—A solution of diazomethane in ether was added in excess to 0.3 g. of the dibasic acid containing acetic acid of crystallization. On evaporation of the ether an oil remained which soon solidified. It was soluble in methyl alcohol and acetone and only slightly soluble in petroleum ether, but crystallized well from 60–70° ligroin. After two crystallizations it melted at 158–159°; $[\alpha]^{22}_{D}$ − 39.1, $[\alpha]^{22}_{546.1}$ − 46.5. These rotations were microdeterminations which are not as accurate as the macro determinations made on the diketone and ketodibasic acid. Titration showed the product to contain no free carboxyl groups.

Anal. Calcd. for $C_{25}H_{38}O_3(COOCH_3)_2$: C, 69.02; H, 8.78; sap. equiv., 252.2. Found: C, 68.76; H, 8.55; sap. equiv., 256.5.

The acid recovered from the determinations of saponification equivalent did not depress the melting point of the original ketodibasic acid.

Summary

A tentative structural formula for chlorogenin is proposed which is based on the products of oxidation with dichromic acid.

STANFORD UNIVERSITY, CALIF. RECEIVED APRIL 5, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

Identification of Alcohols by 3-Nitrophthalic Anhydride[1]

BY G. M. DICKINSON, LEO H. CROSSON AND J. E. COPENHAVER

The use of 3-nitrophthalic anhydride as a reagent for the identification of alcohols was suggested by Nicolet and Sachs,[2] who prepared esters from this acid with nine of the lower alcohols. Ashdown and Monier[3] gave an extensive discussion of the use of this reagent at the Atlanta Meeting of the American Chemical Society in 1930. There has been much study of the higher alcohols within the last few years and it was thought that an extension of this series would be of interest.

The general procedure of the above workers was followed for the preparation of the acid anhydride reagent and the lower esters, but it was found that certain modifications were necessary for the higher derivatives. Their work and that of others showed that the 2-mono-alkyl esters were the principal product and that the 3-mono-alkyl esters were eliminated by crystallization.

Esters of the lower, less expensive alcohols were prepared by heating 3 g. of 3-nitrophthalic anhydride with approximately 2.5 g. of the alcohol and refluxed in a 50-cc. Erlenmeyer flask for one hour. The same quantities were used up to nonyl alcohol but with the increase in the boiling point of the alcohols, they were heated to 100° for two hours to ensure better esterification. From *n*-decyl to *n*-octadecyl, 3 g. of 3-nitrophthalic anhydride and one of alcohol were dissolved in purified toluene and refluxed for three hours.

Recrystallization of the Esters

As shown by Nicolet and Sachs, the esters from methyl to *n*-butyl were recrystallized from water without hydrolysis.

Upon the addition of water and warming, the esters above propyl separated as oils, which, up to and including *n*-hexyl, crystallized on cooling.

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(1) This is an extract from the theses presented by Messrs. Dickinson and Crosson in partial fulfilment of the requirements for the Master of Science degree at the University of South Carolina.

(2) Nicolet and Sachs, THIS JOURNAL, **47**, 2348 (1925).

(3) Ashdown and Monier, *Ind. Eng. Chem.*, *News Ed.*, **8**, No. 6, 6 (1930).

The excess anhydride was decomposed by the water and it was separated as the acid by decantation from the insoluble esters, due to its solubility of 2.05 g. per 100 g. of water. Several solvents were tried but a 30% ethyl alcohol solution was found most satisfactory for esters from *n*-amyl to *n*-heptyl. The concentration had to be increased to 40% for octyl and nonyl. For the lower alcohols, three or four recrystallizations gave constant melting points, but for the higher esters it was necessary to repeat the treatment. Those esters prepared in toluene were separated from the solvent by vacuum distillation and the excess anhydride was removed by warming with 300–400 cc. of water. It was found that the best method to cause these to crystallize was to dissolve them in 95% alcohol, cool slowly and dilute to about 50%, taking care that none of the ester separated as an oil. This process was continued until a constant melting compound was obtained. Higher melting points were obtained by cooling the compounds in a desiccator. The yields of the lower alcohols averaged around 70% and for the higher ones from 60–65%.

Ester	M. p., (corr.), °C.	Molecular weight Calcd.	Molecular weight Found
Methyl[a]	152.9–153.4	...	...
Ethyl	157.7–158.3	239.1	239.7
n-Propyl	144.9–145.7	...	...
Isopropyl	153.9–154.3	253.1	253.6
n-Butyl	146.8–147.0	267.1	267.5
Isobutyl	179.9–180.6	267.1	267.3
s-Butyl	130.6–131.4	...	...
n-Amyl	136.2–136.4	281.1	281.2
Isoamyl	163.2–163.4	281.1	280.7
n-Hexyl	123.9–124.4	295.1	295.2
n-Heptyl	126.9–127.2	308.2	308.5
n-Octyl	127.8–128.2	323.2	323.5
n-Nonyl	124.8–125.2	337.2	336.8
n-Decyl	122.7–122.8	351.7	351.7
n-Undecyl	123.2–123.3	365.2	366.1
n-Dodecyl	123.9–124.0	379.2	379.0
n-Tridecyl	124.0–124.2	393.3	393.8
n-Tetradecyl	123.2–123.5	407.3	407.1
n-Pentadecyl	122.4–122.6	...	...
n-Hexadecyl	121.4–122.0	...	...
n-Heptadecyl	121.0–121.8	449.3	449.4
n-Octadecyl	118.3–119.2	...	...

[a] Nicolet and Sachs reported on the following esters listed above: Methyl, 152–153°; ethyl, 156–157°; *n*-propyl, 141–142°; isopropyl, 152–153°; *n*-butyl, 146–147°; isobutyl, 182–183°; isoamyl, 165–166°.

There is not as great a difference in the melting points of the higher esters as might be desired to absolutely distinguish them from a near homolog but they are of value in checking with other methods. Mixed melting points of adjacent esters above decyl alcohol gave a lowering of 3 to 5°.

The melting points were determined in a 200-cc. round-bottomed flask with a side-tube for insertion of thermometer. Standard Anschütz thermometers, graduated in 0.1 and 0.2°, were used and the bath was stirred by a motor at such a rate to ensure uniform distribution of heat. These precautions gave corrected melting points. The melting point range was taken from the point the compound softened and began sliding down the tube to complete melting. The molecular weights were determined by titrating the esters, dissolved in 50% alcohol, against 0.1 normal sodium hydroxide.

The alcohols from methyl to butyl were carefully distilled with a standard thermometer over a 1° range. *n*-Butyl was donated by the Commercial Solvents Corporation, amyl to heptyl were purchased from Eastman Kodak Company, and for octyl to octadecyl, the authors are indebted to Dr. E. Emmet Reid of Johns Hopkins University. All alcohols above butyl were used without further purification.

COLUMBIA, S. C. RECEIVED APRIL 28, 1937

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 578]

The Structure of Diborane

BY S. H. BAUER

For over a decade numerous structural representations for diborane have been postulated.[1] Unfortunately, the large body of experimental data regarding this substance which accumulated during that period did not permit an unambiguous selection. Only within the past few years has it been realized that the existence of diborane may be accounted for without the introduction of *ad hoc* hypotheses; theoretical justifications based on the currently accepted theories of valence have been formulated[2] favoring the structure initially proposed by Sidgwick.[3] If the assumption relating interatomic distance in molecules with the corresponding "bond-type" be accepted,[4] a determination of the spatial arrangement of the atoms in diborane would lead to definite conclusions regarding its structure. Such a determination was undertaken and successfully carried through by means of an electron diffraction experiment on the vapor.

The Sample.—The diborane used in this investigation (32 cc. of the gas at S. T. P.) was prepared by Dr. Anton B. Burg at the University of Chicago according to the method devised in that laboratory,[5] purified by fractional condensations, and sent to Pasadena by air mail. Since the thermal decomposition of diborane has an induction period of several days, very little decomposition could have taken place during the time of transit (*circa* twenty-six hours) during which the sample was at room temperature. This was substantiated by the fact that no non-condensable material was found on opening the tube. Had some decomposition taken place among the resulting products there would have been hydrogen (the others—B_4H_{10}, B_5H_{11}, B_5H_9, $B_{10}H_{14}$, and non-volatile solids). The container was placed in liquid air immediately upon arrival and kept at that temperature except during the runs which lasted about twenty minutes during which the gas was permitted to warm up to temperatures in the neighborhood of $-72°$. All manipulations were carried out according to standard borane technique.

The Photographs.—Using electrons of λ 0.0613 Å., twelve photographs of varying density were obtained showing five to seven rings. The general qualitative features are sketched in Fig. 1. The similarity of the pattern produced by diborane to the one produced by ethane should be noted. Except for a change in the s-scale (due to the larger dimensions of the borane molecule its entire pattern is compressed) the two are identical; both have a faint inner peak followed by a shallow minimum and two poorly resolved intense maxima, the last appearing more like a shelf. The next minimum is deep; the fourth peak is of medium intensity and has a shoulder on the further side; there then follow several troughs and peaks in decreasing intensity somewhat regularly spaced. The contrast with the features presented by the ethylene photographs is apparent.[6]

Analysis.—The visually determined values of s [$= (4\ \pi \sin \theta/2)/\lambda$] for the apparent maxima and minima are given in Table I. These are the averages of measurements made by three observers. In the last column the ratios of the corresponding s-values for ethane and diborane are given. Since the measurements on the two sets

TABLE I

Max.	Min.	*I*	Wt.	$s_{\text{obsd.}}$	s_{model} B_1	B–B	B–H	$\frac{s_{C_2H_6}}{s_{B_2H_6}}$
2		17	24	5.44	5.89	1.906	1.300	1.13
	3		24	6.53	6.90	1.860	1.268	1.15
3		15	24	7.59	7.82	1.813	1.236	1.19
	4		48	9.13	9.48	1.827	1.246	1.18
4		10	48	10.62	11.32	1.876	1.279	1.18
4a		6	(20)	11.87				
	5		37	13.46	14.53	1.899	1.295	
5		5	37	14.93	16.15	1.904	1.298	1.17
	6		11	16.67	17.33	1.830	1.248	
6		2	17	18.14	18.38	1.783	1.216	1.18
7		1	(4)	21.82				
Weighted mean						1.862	1.270	
Weighted mean dev.						0.031	0.023	
When curve B_2 is used:								
Weighted mean						1.859	1.268	
Weighted mean dev.						0.036	0.025	
When curve D is used:								
Weighted mean						1.852	1.283	
Weighted mean dev.						0.030	0.021	

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(1) For a review of the present status of the problem see Egon Wiberg, *Ber.*, **69**, 2816 (1936). An extensive key to the literature is given.

(2) L. Pauling, THIS JOURNAL, **53**, 3225 (1931); R. S. Mulliken, *J. Chem. Phys.*, **3**, 635 (1935).

(3) N. V. Sidgwick, "The Electronic Theory of Valence," Oxford University Press, London, 1929, p. 103.

(4) Although this criterion has never been stated explicitly, it forms the basis upon which the structural interpretations made by L. Pauling and his collaborators rest, and is implied in the numerous publications by this school which have appeared in recent years. Experimental justification may be found in the *general* constancy of covalent radii except where theoretical deductions lead one to expect discrepancies. Compare, for instance: L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling, L. O. Brockway, and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

(5) H. I. Schlesinger and A. B. Burg, *ibid.*, **53**, 4321 (1931).

(6) Unpublished data on the hydrocarbons were placed at the disposal of the author by Professor L. Pauling, to whom sincere thanks are expressed.

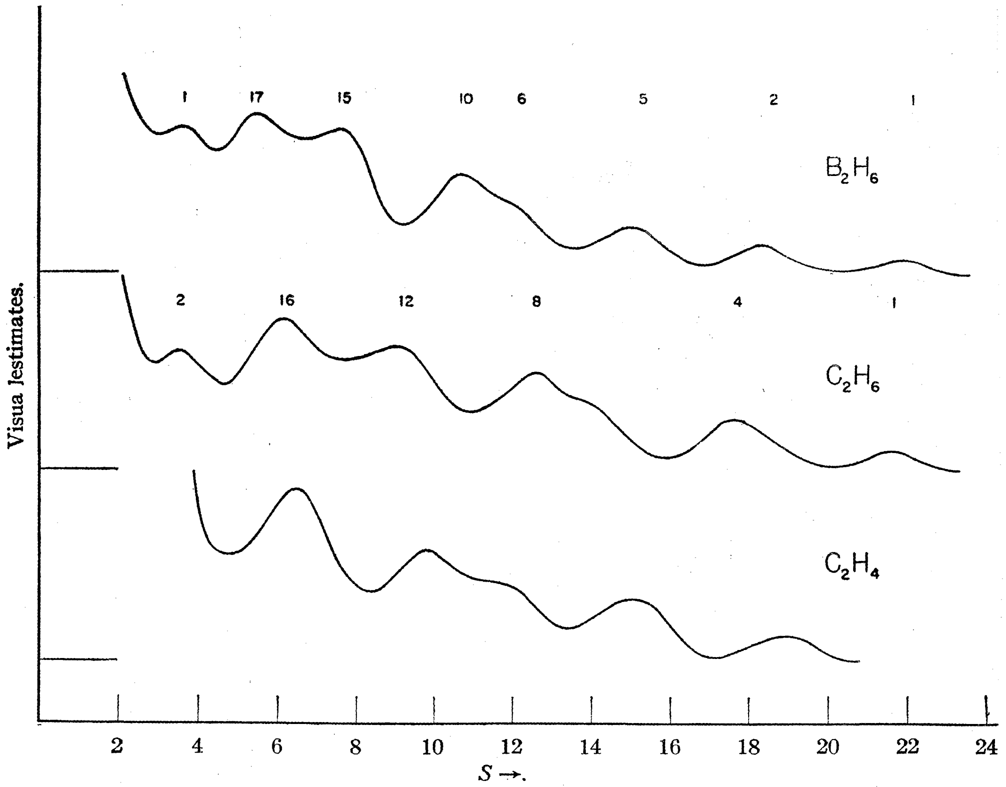

Fig. 1.—Curves representing visual appearance of electron diffraction photographs.

were made by different observers, one would not expect the inner rings to give reliable ratios due to the varying St. John effect. As s gets larger, this ratio assumes the essentially constant value 1.18. An estimate for the B–B separation can thus be made immediately. If the C–C distance in ethane is taken to be 1.55 Å., the corresponding distance in diborane would be roughly 1.55 × 1.18 = 1.83 Å. The above conclusions are in complete accord with the X-ray data on rystals of these two substances vith regard both to the simiarity of the structures and to he interatomic distances.[7]

Results of a six term radial stribution calculation using e tabulated intensities and s-lues are plotted in Fig. 2. e prominent internuclear arations indicated are 1.32, 1.79, and 2.59. is is as good as may be expected from the application of the highly simplified procedure[8] to so light a molecule.

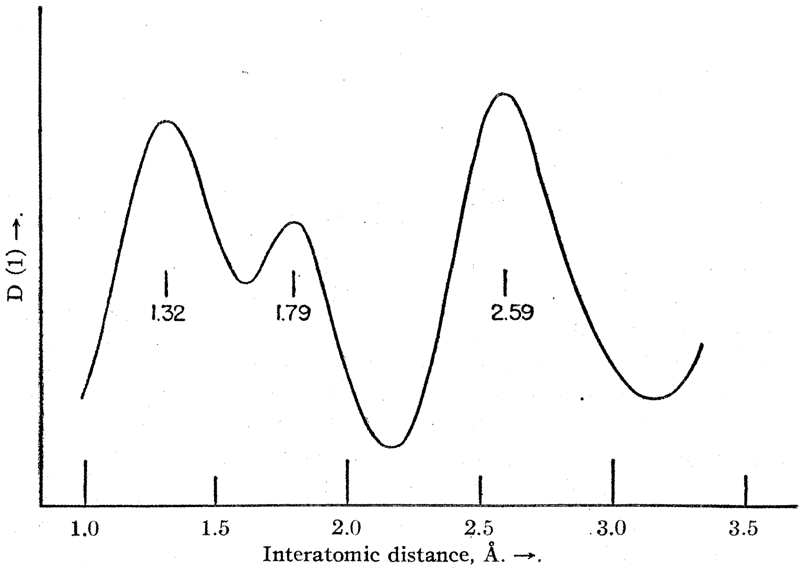

Fig. 2.—Radial distribution curve for diborane.

Theoretical intensity curves using the expression $I = \sum_{ij} Z_i Z_j \frac{\sin l_{ij} s}{l_{ij} s}$ were calculated for various

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) H. Mark and E. Pohland, *Z. Krist.*, **62**, 103 (1925).

[8] L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935).

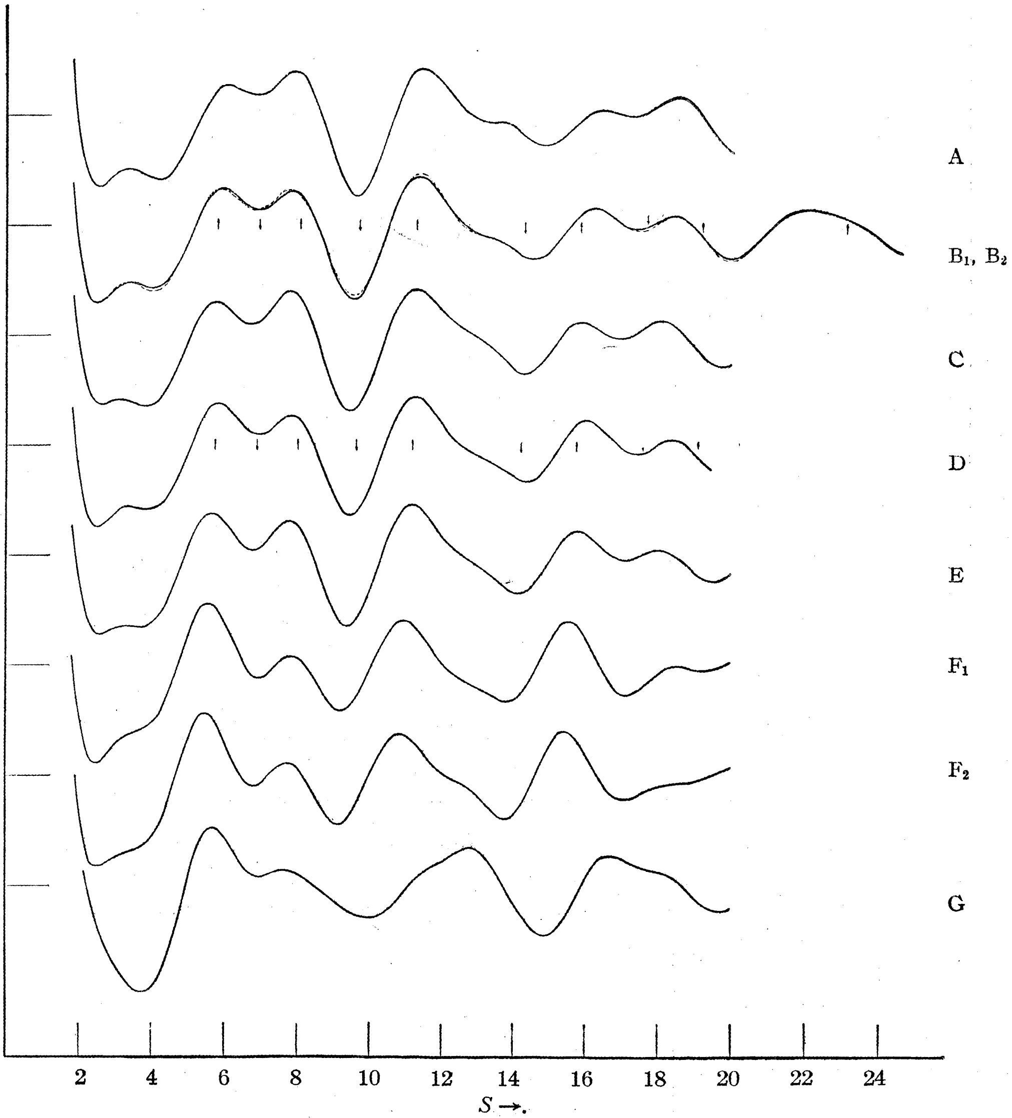

Fig. 3.—Calculated intensity curves. Arrows show best fit with measured ring diameters for models B and D, as obtained from Table I. Curve B_1 is full; B_2 is dashed.

models. Except where explicitly stated, the *cis* (sym. D_{3h}) and *trans* (sym. D_{3d}) orientations were given equal weight. Comparisons of curves B_1 and B_2 conclusively show that the effects on the pattern of free or hindered internal rotation are negligible.[9] In all the models the B–B distance was assumed to be 1.76 Å. except in model G, where it was taken to be 10% less. The curves are shown in Fig. 3.

Model A: Ratio (B–B/B–H) = 1.503 with all angles taken to be tetrahedral.

Eliminated, due to (1) improper intensity relationships between peaks 2 and 3, 5 and 6; (2) prominence of should on the right side of peak 4.

Model B: Ratio = 1.466 with all angles tetrahedr

For curve B_1 (full) equal weights were taken for the and *trans* forms.

For curve B_2 (dashed) only the *trans* position was c sidered.

This model was accepted as the one which gives the qualitative and quantitative agreement with the exp mental data.

Model C: Ratio—the same as for B. The B– angles were assumed to be 113°.

Eliminated, due to (1) improper intensity relation between peaks 2 and 3; (2) the particularly large qua tive discrepancies at the outer rings.

Model D: Ratio = 1.442 with all angles tetrahed

Although this model reproduces very well most qualitative features of the observed diffraction patter

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[9] For ethane, experimental evidence is available that a potential barrier of the order of 2000–3000 calories restricts freedom of rotation of the methyl groups. See J. D. Kemp and K. S. Pitzer, This Journal, **59**, 276 (1937); J. B. Howard, *Phys. Rev.*, **51**, 53 (1937).

shoulder on the right of peak 4 is too faint. The differences between the final interatomic distances as derived from this model and those obtained from B_1 are of the order of 0.01 Å. (Table I) and hence are well within the experimental error.

Model E: Ratio = 1.431, with the B–B–H angles assumed to be 113°.

Eliminated, due to very poor quantitative agreement at large *s* values.

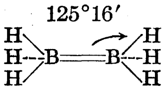
Model F: Ratio = 1.353.

For curve F_1 all angles were assumed to be tetrahedral.

For curve F_2 the B–B–H angles were assumed to be 112°.

Eliminated, due to distinct lack of qualitative and quantitative agreement with data. Model F_2 is the one obtained by taking the distances indicated by the radial distribution curve to correspond to B–H (bonded), B–B, and B–H (non-bonded), respectively.

Model G: Ratio = 1.352. An ethylene-like arrangement with two extra protons.

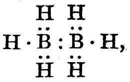


Eliminated, due to the obvious lack of correspondence with the data.

I found it difficult to construct a spatial model which would correspond unambiguously to the structure proposed by Wiberg.[1] If the distribution of H nuclei is the same as in ethane but with two boron atoms connected by a double bond, the ratio (B–B/B–H) would equal 1.351, *i. e.*, essentially model F_1 which may be eliminated as indicated. If the hydrogen atoms are distributed as shown in model G, the Wiberg structure may be equally well discarded. Indeed, it appears impossible to formulate a model having the two boron atoms doubly bonded which would result in a molecule large enough to produce diffraction rings of the observed diameters. Unfortunately the rings are not sufficiently sharp to warrant treating the data by means of the analytic method.[10]

Comparison of the various theoretical intensity curves with the one observed (Fig. 1) eliminates models A, C, E, F, and G. D has the defect of not indicating a sufficiently prominent shoulder on peak 4, whereas B reproduces well all the qualitative features of the observed pattern and is in good quantitative agreement with the data (Table I). This model corresponds to an ethane-like structure with the ratio of (B–B/B–H) equal to 1.466. From the values of $s_{\text{obsd.}}$ and $s_{\text{calcd.}}$ the following conclusions regarding the dimensions of diborane are deduced: (a) The atoms are arranged in the form of two pyramids (axes coincident), their apices, at which the boron atoms are located, pointing toward each other. (b) The B–B distance is 1.86 ± 0.04 Å.; the B–H distance is 1.27 ± 0.03 Å. (The probable errors indicated were taken somewhat larger than the weighted mean deviation as calculated in Table I.) (c) The valence angles of the boron atoms are tetrahedral to within three degrees. The correspondence of these results with the ones obtained through the comparison of the patterns of ethane and diborane should be noted.

Discussion.—The nuclear configuration found for diborane by the electron diffraction method can be immediately interpreted in terms of the nature of the bonds in the molecule. This is done below; a further more detailed description of the electronic structure of the molecule from the valence-bond and the molecular-orbital points of view is also given, followed by a discussion of the chemical and physical properties of the substance.

The tetrahedral radius for a boron atom with a completed octet has been assigned the value 0.89 Å.,[11] from extrapolation of the sequence F, O, N, C; this value is also indicated by the comparison of BH with CH and other diatomic hydrides. We accordingly would expect for the B–B and B–H single bond distances 1.78 and 1.18 Å., respectively. In the two cases which have been studied experimentally the boron atoms did not possess completed octets, yet dimensions of this order or somewhat smaller were observed; thus the B–B distance in CaB_6 is 1.716 Å.,[12] and in B_5H_9 an average value of 1.76 Å. is obtained.[13] In the molecule BH the B–H separation is found to be 1.226 Å. While it is generally true that in the diatomic hydrides the internuclear distance is greater than in the corresponding polyatomic hydride molecules (C–H = 1.09 in CH_4, 1.12 in CH), in diborane the situation is reversed. *Actually, the values for the B–B and B–H distances in* B_2H_6 *are both considerably larger than the single-bond separations, showing that all the bonds in the molecule have to some extent the character of bonds weaker than "single" bonds.* This is expected for the B–H bonds on the basis of Sidgwick's structure  $\begin{matrix} & \mathrm{H} & & \mathrm{H} & \\ \mathrm{H}\cdot & \ddot{\mathrm{B}} & : & \ddot{\mathrm{B}} & \cdot\mathrm{H} \\ & \ddot{\mathrm{H}} & & \ddot{\mathrm{H}} & \end{matrix}$, which gives each B–H two-thirds single-bond and one-third one-electron-bond character; a slight extension of this configuration considering resonance to structures such as

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[10] S. H. Bauer, *J. Chem. Phys.*, **4**, 406 (1936).

[11] L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[12] L. Pauling and S. Weinbaum, *ibid.*, **A87**, 181 (1934).

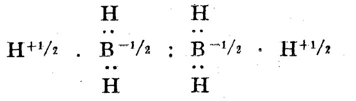
[13] S. H. Bauer and L. Pauling, THIS JOURNAL, **58**, 2403 (1936).

$\mathrm{H}\cdot\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}\cdot\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}:\mathrm{H}$ also would further account for the observed increase of the B–B bond distance. The observed distances are equally compatible with Lewis' structure, representing resonance among the seven arrangements $\mathrm{H}:\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}\ \underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}:\mathrm{H}$, $\mathrm{H}\,\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}:\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}:\mathrm{H}$, etc., and giving each bond $^6/_7$ single-bond character and $^1/_7$ no-bond character. However, strong theoretical arguments may be given to support the view that *the molecule resonates among all the structures of the Sidgwick and Lewis types*, the B–B and the B–H bonds having single-bond, one-electron-bond, and no-bond character.

It is especially significant that shortening the B–B distance below the single-bond value, as would be required for any structure giving the B–B bond some double-bond character, is not observed. This eliminates all structures such as Wiberg's.

In the language of atomic orbitals the structure of diborane should therefore be described as follows: The allowed orbitals for boron are four in number, of the hybridized sp^3 type, directed toward the corners of a tetrahedron. Each of these may be occupied by a shared electron-pair, by a single electron, or left empty. Thus the valence-bond configurations which contribute to the ground state are (formal charges indicated):

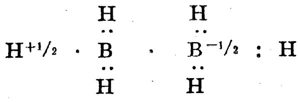
I



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{H}^{+1/2} & . & \mathrm{B}^{-1/2} & : & \mathrm{B}^{-1/2} & \cdot & \mathrm{H}^{+1/2} \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

(9)

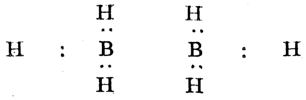
II



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{H}^{+1/2} & \cdot & \mathrm{B} & \cdot & \mathrm{B}^{-1/2} & : & \mathrm{H} \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

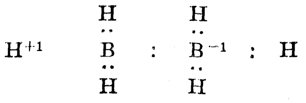
[14] (6)

III



$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & \cdot\cdot & & \cdot\cdot & \\ \mathrm{H}\ : & \mathrm{B} & & \mathrm{B} & :\ \mathrm{H} \\ & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

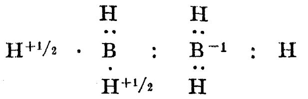
IV



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{H}^{+1} & & \mathrm{B} & : & \mathrm{B}^{-1} & : & \mathrm{H} \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

(6)

V



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{H}^{+1/2} & \cdot & \mathrm{B} & : & \mathrm{B}^{-1} & : & \mathrm{H} \\ & & \cdot & & \cdot\cdot & & \\ & & \mathrm{H}^{+1/2} & & \mathrm{H} & & \end{array}$$

(6)

so that the wave function of diborane may be represented approximately by a linear combination of the wave functions of the above structures. The question as to their relative weights will be discussed later; nevertheless, it is evident that the contributions of the structures II and III will tend to weaken the B–B bond. Combination of II and IV alone gives the arrangement proposed by G. N. Lewis.[15] His description requires that all the electrons remain paired but not that they occupy all the orbitals simultaneously. Through this argument he was led to predict the diamagnetism and characteristic weak bonds of diborane.

Although the individual members of the structural types II, IV, and V do not have the symmetry which we associated with diborane (D_{3d}),

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(14) Justification for writing structures of type I, that is, configurations involving a one-electron bond between B_2H_5 and H, has already been presented [L. Pauling, THIS JOURNAL, **53**, 3225 (1931)]. Professor Pauling then estimated that the coulomb attraction, at small distances, of $B_2H_5^-$ and H^+ may contribute as much as 10 or 11 volts to the energy of the aggregate. In order to justify structures of type II wherein a one-electron-bond is placed between the two BH_3 groups one must show that the systems (a) $BH_3^+ + BH_3^-$ (when in valence state), and (b) $BH_3 + BH_3$ (when in valence state) have energies which are nearly equal at small internuclear separations. The following rough estimates indicate that this is the case.

In (a): The ionization potential of a BH_3 radical when in its ground state ($[sa_1]^2\ [\pi e]^4$, $^1A_1$) may be taken equal to 12.6 volts. This value was suggested by Prof. Mulliken on the ground that the energy of removal of a $[\pi]$ electron (B–H bonding) should be approximately the same when in a free BH_3 group as when in B_2H_6. The configuration of the ion is $[sa_1]^2\ [\pi e]^3$. On the other hand, the electron affinity of a BH_3 radical (closed shell structure) must be rather close to zero; the capture of an electron leads to the ion BH_3^-, $[sa_1]^2\ [\pi e]^4\ [\sigma a_1]$. If the contribution of the coulomb energy of the two ions at small separations is taken to be ten volts, as in the case of $B_2H_5^-$ and H^+, the energy of the resulting aggregate is in the neighborhood of 2–3 volts above that of two BH_3 ($^1A_1$) groups. On very close approach these will combine to form the molecule B_2H_6, $[sa_1]^2\ [sa_1]^2\ [\pi e]^4\ [\pi e]^3\ [\sigma + \sigma, a_{1g}]$, $^{1,3}E_g$, etc. If a $^1A_1$ state is desired for the final diborane the process which must be followed is described schematically

$$\left.\begin{array}{l} \mathrm{BH_3(^1A_1)} \xrightarrow{12.6\mathrm{v}} \mathrm{BH_3}^+,\ ([sa_1]^2\ [\pi e]^3 \xrightarrow{4\mathrm{v}} \\ \qquad\qquad\qquad\qquad (\mathrm{BH_3}^+)^*,\ ([sa_1]\ [\pi e]^4) \\ \\ \mathrm{BH_3(^1A_1)} \xrightarrow{0\mathrm{v}} \mathrm{BH_3}^-,\ ([sa_1]^2\ [\pi e]^4\ [\sigma a_1]) \end{array}\right\} \xrightarrow{-10\mathrm{v}}$$

$$\underbrace{(\mathrm{BH_3}^+)^* + \mathrm{BH_3}^-}_{\text{is approximately seven volts above two } \mathrm{BH_3}\ (^1\mathrm{A_1}) \text{ groups.}} \longrightarrow (\mathrm{B_2H_6})^*,\ [sa_1]\ [sa_1]^2\ [\pi e]^4\ [\pi e]^4\ [\sigma + \sigma, a_{1g}],\ {}^1\mathrm{A_{1g}}, \text{ etc.}$$

In (b): Since the combination of two BH_3 radicals results in repulsive states only, it is necessary to excite one of them to the configuration $(BH_3)''$, $[sa_1]^2\ [\pi e]^3\ [\sigma a_1]$. This process requires an energy equivalent to 2–3 volts. Hence the resulting aggregate is near in energy to that obtained above from the close approach of the unexcited ions, *i. e.*, leading to B_2H_6, $^{1,3}E_g$, etc. Again, if a $^1A_1$ state is desired for the diborane molecule, the corresponding schematic process is

$$\left.\begin{array}{l} \mathrm{BH_3(^1A_1)} \xrightarrow{2\text{–}3\mathrm{v}} (\mathrm{BH_3})'',\ ([sa_1]^2\ [\pi e]^3\ [\sigma a]) \xrightarrow{4\mathrm{v}} \\ \qquad\qquad\qquad\qquad (\mathrm{BH_3})''^*,\ ([sa_1]\ [\pi e]^4\ [\sigma a]) \\ \mathrm{BH_3(^1A_1)} \end{array}\right\} \xrightarrow{0\mathrm{v}}$$

$$\underbrace{(\mathrm{BH_3})''^* + \mathrm{BH_3}}_{\text{is approximately 6–7 above two unexcited } \mathrm{BH_3} \text{ groups.}} \longrightarrow (\mathrm{B_2H_6})^*,\ {}^1\mathrm{A_{1g}}, \text{ etc.}$$

(15) G. N. Lewis, *J. Chem. Phys.*, **1**, 17 (1933).

symmetric and antisymmetric linear combinations of the six components of each type will result in two configurations of equal energy, one of which (the symmetric) may be used in further combinations with I and III. The latter interaction will cause the energy of the over-all symmetric combination to be lowered and of the remaining antisymmetric one to be raised, so that the ground state of diborane will be of the A_1 type. Let us now attempt to deduce its multiplicity. Structures III and IV are in singlet states; I, II, and V may have the spins of the electrons participating in the one-electron-bonds either parallel or antiparallel, but only when in the latter arrangement are the structures permitted to combine with III and IV.[16] The relative energies of the singlet and triplet states of the structures belonging to the Sidgwick configuration will vary with the different types, but this we cannot estimate in the present treatment. However, since the interaction of the structures having resultant spin zero with the ones belonging to the Lewis configuration will give a state whose energy is lower than that of either configuration alone, we may conclude that the ground state will be singlet, *i. e.*, that diborane has a ground state ($^1A_1$) which is diamagnetic, as observed, and a low-lying paramagnetic state ($^3A_2$) whose existence has not yet been verified.

Professor Mulliken has already given a molecular orbital treatment of this and related molecules.[2] The present data make possible unambiguous decisions for several questions arising in that discussion, the answers for which heretofore could be only surmised. Very roughly, the following configurations may be correlated with the various structures listed above[17] (omitting the 1s electrons of boron):

IM $[s + s, a_{1g}]^2\ [s - s, a_{2u}]^2\ [\sigma + \sigma, a_{1g}]^2\ [\pi e]^3\ [\pi e]^3$, $^1A_{1g}$, etc. with I

IIM $[s + s, a_{1g}]\ [s - s, a_{2u}]^2\ [\sigma + \sigma, a_{1g}]\ [\pi e]^4\ [\pi e]^4$, ^1A_1g, etc. with II

IIIM $[sa_1]^2\ [sa_1]^2\ [\pi e]^4\ [\pi e]^4$, $^1A_{1g}$ with III

IVM $[s + s, a_{1g}]^2\ [s - s, a_{2u}]^2\ [\sigma + \sigma, a_{1g}]^2\ [\pi e]^4\ [\pi e]^2$, $^{1,1}A_{1g}$, etc. with IV + V

where the $[\sigma + \sigma]$ electrons are mainly B–B bonding and the others are essentially confined to the B–H bonds (the $[s + s]$ electrons also contribute to the B–B bond).

It will be noted that whole-molecule orbitals were written for the $[sa_1]$ electrons in IM, IIM, and IVM, whereas this was not done for the $[\pi e]$ electrons. The reason is evident. Since the former are nearly but not entirely confined to the BH_3 groups, while the $[\sigma + \sigma]$ electrons, although strongly B–B bonding, also assist in the B–H bonds, their wave functions overlap, so that a hydridization (between the $[s + s]$ and $[\sigma + \sigma]$) which becomes possible only after the linear combination of the $[sa_1]$ orbitals is made, would result in a somewhat better representation of the electron configuration. As in ethane, this interaction will cause the $[\sigma + \sigma]$ electrons to have a somewhat lower ionization potential and the $[s + s]$ electrons a correspondingly higher one. Similarly, the use of whole-molecule orbitals $[\pi + \pi, e_u]$, $[\pi - \pi, e_g]$ would indicate a resonance between the $[\pi e]$ electrons of the two BH_3 groups. This would necessitate that the $[\pi]$ bonding be very strong, and that there be considerable overlapping of their wave functions in the region between the boron atoms, introducing effectively a double bond contribution. Each of the BH_3 groups would then have a tendency to be planar. The observed spatial structure is distinctly contrary to such an hypothesis. The B–H as well as the B–B distances are larger than might have been expected even for pure single bonds, and the BH_3 groups are pyramidal. Indeed this state of affairs was anticipated by Mulliken on the basis of the fact that diborane does not have an absorption region in the visible. Hence,[2] his configurations 1a, 2a, and 3a are definitely eliminated. In IIIM the $[sa_1]$ electrons were placed in the radical orbitals since this arrangement corresponds to repulsion between the BH_3 groups.

The question arises whether all the states listed have sufficiently low energies to contribute appreciably to the ground state. By correlating, respectively, the IM and IIIM configurations with the two $^1A_1$ ($[sa_1]^2\ [\pi e]^4$) and two ^3E ($[sa_1]^2\ [\pi e]^3\ [\sigma a_1]$) states of the separated BH_3 groups, Mulliken was able to estimate that the unperturbed levels corresponding to the $^1A_{1g}$ states of IM and IIIM would be approximately one volt apart and that the interaction energy would be of the order of one-half volt. The energy of con-

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[16] For the resonance criteria among several structures see L. Pauling, THIS JOURNAL, **54**, 988 (1932).

[17] For the present, configurations giving rise to $^1A_1$ states will be considered since only these are permitted to interact with the structures which appear to give the largest contribution to the ground state (I and III). The correlations indicated to the right refer to the symmetric linear combinations of the individual members of the particular type.

figuration IVM is probably slightly above that of IM since in going from the latter to the former an electron is merely transferred from a $[\pi]$ orbital of one BH_3 group to the same orbital in the other. State IIM, however, is highly excited. The corresponding unexcited one is given by Mulliken

$$\text{IIM}\ [s+s, a_{1g}]^2\ [s-s, a_{2u}]^2\ [\sigma+\sigma, a_{1g}]\ [\pi e]^4\ [\pi e]^3,\ {}^{1,3}E_g, \text{ etc.}$$

Since the ionization potential of the $[s]$ electrons was estimated at approximately 17 volts while that of the $[\pi]$ electrons only 12.6 volts and of the $[\sigma + \sigma]$ at 13.0 volts,[2,18] IIM lies far above IIm. The latter cannot interact with IM, IIIM, and IVM while the former may but can contribute only slightly to the ground state due to the fact that it is so far removed from the other components. Hence, when diborane is in its lowest energy state, its structure may best be represented by a combination of the configurations IM, IIIM, and IVM with very little of IIM. (IIIM must make an appreciable contribution in order that the large B–B separation may be accounted for.) Let us now return to the atomic orbital treatment and specify that the magnitudes of the coefficients in the linear combination for the wave function of diborane are probably in the order: I, III, IV, and V with very little of II (excited).

The compounds B_4H_{10} and B_5H_{11} which presumably have chain-like structures should have electron configurations, and B–B and B–H distances entirely analogous to those found in diborane, as contrasted with the ring structure of B_5H_9.[13]

Discussion of the Physical Properties.—Four physical constants of diborane have been measured. These are quoted by Wiberg[1] in support of his structure. Let us see how they may be interpreted in terms of the structure given by the electron diffraction study.

(1) **Diamagnetism.**—The ground state of the configuration discussed above is of the singlet symmetric type and hence is diamagnetic.

(2) **Lack of Electric Dipole Moment.**—Both Profs. Pauling and Mulliken stressed the fact that in their formulation (as in the amplified one presented in this paper) all the hydrogen atoms are equivalent. Diborane consequently should have no moment.

(3) **Similarity of Ultraviolet Absorption Spectrum to that of Ethylene.**—The deduction that in diborane the boron atoms are doubly bonded from the similarity of its ultraviolet absorption spectrum to that of ethylene is fallacious. An explanation of the two continuous regions of absorption on the basis of Mulliken's electron configuration (which is essentially the one given in this analysis) has been suggested by E. Blum and G. Herzberg.[19]

Professor Mulliken reports [*J. Phys. Chem.*, February, 1937] that diborane shows no absorption in the near ultraviolet, visible, and photographic infrared (λ2500–λ12,000). This is somewhat puzzling since various low-lying electronic levels to which transitions from the ground state are not forbidden have been predicted.[2]

(4) **Parachor.**—Stock and collaborators made a careful determination[20] of the surface tension and density of diborane. As far as the author is aware, this is the first investigation of its kind which has been carried out on a compound the structure of which must be represented by one-electron-bonds resonating with electron-pair-bonds. Since the contribution to the parachor of any type of bond can only be determined experimentally, one cannot draw any conclusions regarding the structure of this compound from the value of its surface tension. Deductions made from phosphorus and arsenic pentachlorides (which gave the value -12.4, employed by Wiberg, in obtaining the parachor of the Sidgwick structure) are entirely without foundation since most chemists believe that the latter molecules have no "singlet" bonds. However, the work of Stock and collaborators would permit one to calculate an appropriate number which might be used in future structure determinations.

Wiberg admits[1] that the available chemical evidence is in harmony with the Sidgwick configuration. The modifications introduced by Pauling, Mulliken and in the present discussion do not alter this state of affairs. Since the types of bonds found in diborane and its homologs are essentially unlike those in other molecules ordinarily dealt with by chemists one cannot safely reason by analogy. Predictions as to how such molecules behave chemically can be made only after sufficient empirical data have been gathered.

Resonance Energy of Diborane.—The heat of formation of diborane from solid boron and molecular hydrogen was recently determined to

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[18] A similar inequality amounting approximately to eight volts is given for ethane; R. S. Mulliken, *J. Chem. Phys.*, **3**, 517 (1935).

[19] E. Blum and G. Herzberg, *J. Phys. Chem.*, **41**, 91 (1937).

[20] A. Stock, E. Wiberg and W. Mathing, *Ber.*, **69**, 2811 (1936).

be 44 ± 3 kcal.[21] We are now in a position to make an estimate of the resonance energy in diborane. Let us first consider the reaction B(s) + $1^1/_2H_2$ = BH_3(g). Since the electronegativities of boron and hydrogen are identical for purposes of calculation there are no heat effects due to the ionic contributions of the bonds. Hence if the solid consists of boron atoms which are bonded to three others by single bonds it is clear from Pauling's additivity rule that the above reaction will be accompanied by a zero heat effect since for every B–H bond which is formed one-half an H–H and one-half a B–B bond will be broken. On the other hand, it appears quite likely that in the solid the boron atoms are tetrahedrally bonded, thus making use of all the orbitals available to them by means of some resonance scheme; then more bonds will be broken in the vaporization process than will be formed in the hydrogenation. Consequently the reaction giving rise to BH_3 radicals will be endothermic by an amount equivalent to the resonance energy present in solid boron. But the heat of formation of diborane from the elements was found to be exothermic. Hence we must conclude that the reaction $2BH_3 = B_2H_6$ is exothermic to the extent of 44 kcal. if the first alternative is assumed or to the extent of 44 kcal. plus the resonance energy available for each pair of atoms in solid boron if the second is preferred.

The stability of B_2H_6 relative to BH_3 or B_2H_4 is due to the resonance energy made possible in the former compound by the complete use of all the four orbitals permitted to boron atoms. From the arguments presented in the preceding paragraph we may estimate that a minimal value for this energy is 44 kcal. and may be set equal to the latter figure plus the resonance energy for a pair of boron atoms in the solid element.

Acknowledgments.—The author expresses the sincerest appreciation to Dr. Anton B. Burg for providing the sample, to Professor Pauling for numerous helpful discussions, to Dr. L. O. Brockway for the use of his diffraction apparatus, and to Mr. H. Levy for aid in taking the electron diffraction photographs.

Summary

Electron diffraction photographs of diborane indicate that this compound has an ethane-like structure with the B–B distance equal to 1.86 ± 0.04 Å. and the B–H distance 1.27 ± 0.03 Å.; the valence angles of the boron atoms are found to be tetrahedral within three degrees. An electron configuration compatible with the large interatomic distances is presented both in terms of the atomic and molecular orbital modes of description and the conclusion is reached that the stability of B_2H_6 relative to BH_3 is due to the resonance energy made available through the full use of the four orbitals of boron.

PASADENA, CALIF. RECEIVED MARCH 2, 1937

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[21] W. A. Roth and E. Börger, *Ber.*, **70**, 48 (1937).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. III. The Carbon–Hydrogen and Carbon–Carbon Bonds in Propane and Ethylene

BY KIYOSHI MORIKAWA,[1] N. R. TRENNER[2] AND HUGH S. TAYLOR

The present research represents an extension to propane and ethylene of investigations previously reported by Morikawa, Benedict and Taylor dealing with methane[3] and ethane.[4] In the latter communication attention was directed to an abnormally high inhibitory action of hydrogen on the surface hydrogenation decomposition of ethane to yield methane. We have examined in the present work, in a more detailed manner, the kinetic relations of the decomposition and exchange reactions between propane and deuterium with results which confirm and extend our observations with ethane. Isotope exchange reactions with ethylene are also included as well as other supporting studies leading to a general discussion of the whole problem of activation in such hydrocarbon systems.

Experimental Details

Materials.—In addition to those gases described in the previous papers,[3,4] we have employed propane, ethylene

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[1] Visiting Research Fellow of the Central Laboratory, South Manchurian Railway Co., Darien, Japan.

[2] Research Associate, Princeton University.

[3] Morikawa, Benedict and Taylor, THIS JOURNAL, **58**, 1445 (1936).

[4] Morikawa, Benedict and Taylor, *ibid.*, **58**, 1795 (1936).

and propylene. In each case the gases were obtained from cylinder supplies and purified by repeated fractionation. With propane the only likely impurity in the purified sample would be a trace of butane. The ethylene was 100% C_2H_4 within the analytical error. The propylene analyzed 98% C_3H_6, 2% C_3H_8.

Experimental Method.—A static method was employed, essentially the same as that described in Part II but of $\sim$135 cc. reaction volume. After definite reaction times the products were removed by a Töpler pump. About 95% of the gas could thus be removed within five minutes, but fifteen minutes were required to remove all the gas. Temperature control of the reaction was by means of vapor baths.

Analytical Procedure.—Hydrogenation decomposition was followed by the increase in saturated hydrocarbon, $+\Delta$H.C. after removal of hydrogen by combustion over copper oxide at 230°. In some cases, a fractionation method was employed to define the composition of the hydrocarbon products.

The isotope exchange reaction was followed by a determination of the C–D content of the *hydrocarbons*. This was checked occasionally by the D content of the hydrogen. Both analyses were made with a thermal conductivity gage to be described elsewhere.[5] An accuracy of 0.5% in the analyses of the ethanes and propanes and 0.1% for the hydrogens was possible.

Propane and ethane were separated from hydrogen by passage through a liquid-air trap. Traces of hydrogen were removed from the condensate by repeated vaporizations, freezings and evacuations at liquid-air temperature. The final purification of the gases for analysis was by fractional distillation under reduced pressure ($\sim$2 mm.). Details of this fractionation technique will be described in a separate communication[6] since it has general applicability and is essential to our method of analysis by thermal conductivity.

Experimental Results

Exchangeable Hydrogen in a Nickel–Kieselguhr Catalyst.

—It was necessary to determine the extent to which deuterium would exchange with hydrogen sources in a nickel–kieselguhr catalyst in the ranges of temperature in which exchanges with hydrocarbons occur. Two series of experiments detailed in Table I were performed. The same catalyst, 2 g. in weight, $\sim$ 15% Ni, was used in both series. The catalyst was prepared from nickel carbonate precipitated on kieselguhr, by reduction for four hours at 425° followed by evacuation with a mercury diffusion pump system for two hours at the same temperature. Between each experiment the catalyst was washed thoroughly with hydrogen at the reaction temperature and then evacuation, for intervals of time noted in the table, followed. Then $\sim$23 cc. of deuterium was introduced. After definite time intervals the gas was recovered by a Töpler pump and analyzed on the thermal conductivity gage. The experiments in Series II were made after the catalyst had been changed in activity by heating to 500° with evacuation.

These experiments lead to the following conclusions. From Expts. 51 and 52 it is evident that one hour of evacuation is adequate and that equilibrium is also established in one hour. From Expts. 58 and 59 we conclude that thirty-six minutes is not sufficient for equilibrium at 302°. Experiments 53 and 60 show that evacuation at 302° decreases the hydrogen content by 5.5%, but this is still only a fraction of the hydrogen available at 98°. On the other hand, it removes all of the hydrogen available at 55° (see Expts. 104 and 111).

TABLE I

HYDROGEN SOURCES OF NICKEL–KIESELGUHR CATALYST

Order of expt. no.	Temp. of washing and evacuation, °C.	Time of last evacuation, hrs.	Reaction Temp., 0° C.	Time, hrs.	D_2 introduced, cc.	Gas recovered, cc.	D content of recovered gas, %	Amt. of H_2 source (K = 1), cc.
Series I								
51a	55	7.5	55	8.3	22.9	21.3	83.4	4.3
b	55	..	55	1.0	22.9	23.1	96.0	..
52a	55	1.0	55	1.0	23.3	22.6	83.0	4.5
b	55	..	55	2.0	23.0	22.9	95.0	..
53	98	3.1	98	1.0	22.9	21.7	82.0	4.8
54	138	2.0	138	1.0	23.2	22.3	76.9	6.7
55	172	2.8	172	1.0	23.4	21.8	71.7	8.9
56a	218	2.0	218	1.0	23.1	21.9	58.8	15.8
b	218	..	218	1.5	23.2	23.2	82.4	..
c	218	..	218	1.0	22.8	22.8	90.7	..
57	255	2.0	255	0.6	23.3	22.4	53.8	19.7
58	302	2.0	302	.6	23.7	22.9	44.3	30.1
59	302	2.1	302	5.2	23.5	22.5	38.9	36.4
60	302	2.0	98	4.0	22.9	19.6	87.5	3.0
Series II								
102	450	4.0						
	500	4.0	218	3.5	23.2	19.1	69.8	9.7
103	218	2.0	218	2.0	23.6	22.5	69.7	9.8
104	55	2.0	55	2.0	23.1	22.0	86.2	3.3
110	0	2.0	0	2.0	23.6	22.8	86.2	3.4
111	302	2.0	55	2.0	23.6	20.3	96.2	0.6

Experiments labelled a, b, c referred to successive experiments without intermediate washing and evacuation.

From the whole series (51–60) we conclude that the amount of hydrogen available increases as the temperature rises, but that the data detailed above indicate two types of available hydrogen, one readily removed by evacuation at high temperature, the other not so removable.

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[5] N. R. Trenner, *J. Chem. Phys.*, forthcoming paper.

[6] Morikawa and Trenner, THIS JOURNAL, forthcoming paper.

Prior to Expt. 102 four hours of evacuation at 450° yielded 8.4 cc. of water vapor and a further four hours at 500° gave an additional 8.5 cc. After this removal the hydrogen content of the wash gas decreased by 11% at 218° but only by 3% at 55° (*cf.* Expts. 51, 52, 104). From the data of Expts. 102, 103 it is obvious that evacuation at 218° removes all of the more readily available hydrogen.

Assuming an equilibrium constant of 1 between deuterium and the hydrogen source on the catalyst the values for this source are given in the final column of Table I, and represented in curve A, Fig. 1. The calculations are made with the aid of the equation

$$\text{Cc. of available } H_2 = \frac{\text{cc. of } D_2 \text{ introduced (99\% D found)}}{\text{\% D found}}$$

The same volume of hydrogen is recoverable at 218° as at 55°. Experiments detailed in Table II indicate that, in this range of temperature, the activated adsorption of hydrogen decreases as the temperature rises. The amount adsorbed at 0.15 mm. pressure was found to be ~5.5 cc., a value to be compared with 4.5 cc. available at 55° with an evacuation pressure of 10^{-3} mm. as revealed by the exchange reaction. We therefore conclude that the available hydrogen which can be evacuated at 55° is hydrogen gas and that the other available hydrogen which is difficultly removable at higher temperatures results from water. We further conclude that this water does not exist on the nickel surface but is present in the kieselguhr support, the silicates of which hold water with varying degrees of tenacity. These hydrogen sources are quite reproducible and so point to the establishment of equilibria of the type

$$\text{Ni–Kieselguhr } H_2O + D_2 = \text{Ni–Kieselguhr } D_2O + H_2$$

The experimental value of the total available hydrogen at 218° is ~16 cc., which is in agreement with the calculated value of 16 cc. assuming an equilibrium constant $K = 1$. If we use the constant $K = 1.46$ obtained from Farkas' data[7] for the equilibrium between free water and deuterium, a calculated value of 13.6 cc. of available hydrogen would be obtained. We may ascribe the difference in equilibrium constants to the existence of hydrated kieselguhr as the water source.

These conclusions are substantiated by the following two series of experiments. A 2-g. sample of fresh unreduced catalyst was heated to 425° with evacuation and held at that temperature for two hours. It was then cooled and washed with deuterium at room temperature. The catalyst was then gradually raised in temperature in a stream of deuterium to 400°, samples of gas being withdrawn at intervals and analyzed. The deuterium consumed in the reduction was 66.3 cc. and the water frozen out in a carbon dioxide trap corresponded to 60.2 cc. The hydrogen received in the deuterium gas amounted to 16.8 cc. The hydrogen content of the water condensed out was determined by equilibrating the water vapor with deuterium on the catalyst at 138°. In this manner, using $K = 1.46$, we determined in all 22.4 cc. of hydrogen in the water and a total hydrogen in both gas and water of 16.8 + 22.4 = 39.2 cc. If we use $K = 1$ the corresponding amounts are 16.8 + 31 = 47.8 cc., which values determine the upper and lower limits for the total hydrogen.

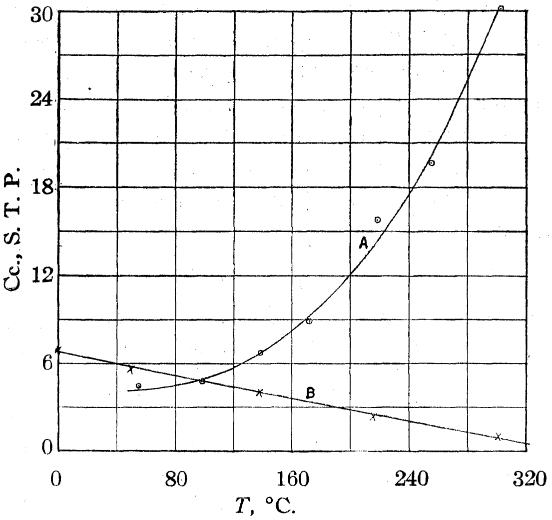

Fig. 1.

The catalyst was then evacuated for two hours at 138° and 56.8 cc. of water vapor was frozen out in the carbon dioxide trap. The catalyst was then well washed with hydrogen at 218° and evacuated for ten hours at the same temperature. The water removed was 7.7 cc., making a total recovered water of 64.5 cc. The close correspondence of this with the deuterium consumption, 66.3 cc., indicates that almost all the water produced in the reduction process could be desorbed at 218°. This implies that the water available in the experiments of the first two series is not water on the nickel surface but in the kiesel-

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(7) Farkas, "Light and Heavy Hydrogen," p. 180, *et seq.*

guhr. This was confirmed by introducing 22 cc. of deuterium gas, equilibrating for three and a half hours at 218° when, after evacuation, the desorbed gas contained only 37% deuterium corresponding to a source of 34 cc. of available hydrogen.

Adsorption Isobars (p ~ 0.15 mm.) of Deuterium on Nickel.—The nickel catalyst was evacuated at a temperature T_1 for about twenty minutes by the Töpler pump and the pressure (P_1) built up in the next thirty minutes was measured. The temperature was then raised to T_2 and the pressure (P_2) was read. The desorbed deuterium (ΔD_2) was measured and the pressure (P_3) built up on standing for one-half hour was noted. These operations were repeated from −83 to 302°. The data obtained are shown in Table II.

TABLE II

ISOBAR OF D_2 ON Ni CATALYST AT ~0.15 MM. PRESSURE

T_1, °C.	P_1 at T_1, mm.	T_2, °C.	P_2 at T_2., mm.	ΔD_2, cc.	P_3 at T_2, mm.
0	0.18	55	2.1	1.39	0.14
55	.14	138	4.0	1.65	.16
138	.16	218	3.2	1.56	.18
218	.18	302	3.8	1.30	.10
−83	.58	23	18.7	5.03	.42
−24	..	22.4	3.9	1.29	.25
−83	.16	21.3	9.1	2.88	.25

Evacuation for twenty minutes with the Töpler pump corresponds approximately to evacuation for five minutes with our mercury diffusion pump train. A plot of deuterium adsorbed against temperature shown in Fig. 1 shows a decreasing hydrogen adsorption with increasing temperature, curve B, Fig. 1.

The Hydrogenation Decomposition of Propane.—The experimental data on the conversion of propane and hydrogen to ethane and methane are collected in Table III.

The original catalyst, as for the experiments in Table I, was used. It will be seen that the reaction acquires an appreciable velocity at 138°, which is about 10° lower than in the case of ethane. The decomposition with deuterium was again slower than that with hydrogen, as with ethane. The fractional analyses of the hydrocarbon products, given in Table IV, shows that the initial reaction yields ethane and methane and that the ethane thus formed decomposes further to methane, but not to an appreciable extent under the majority of our conditions. We, therefore, represent the total over-all reactions, thus

$$C_3H_6 + H_2 = CH_4 + C_2H_6$$
$$C_2H_6 + H_2 = 2CH_4$$

TABLE III

HYDROGENATION DECOMPOSITION OF PROPANE

No.	Propane, cc.	H_2, cc.	Temp., °C.	Time, hrs.	+ΔH.C., %	%ΔH.C. per hr.
36	11.5	23.3	138	10.3	22.9	2.2
35	11.4	22.9	157	3.0	39.3	13.1
37	11.5	23.3	172	1.1	69	63
38	11.4	23.1	184	1.1	⩾190	
39	11.4	23.4	157	3.0	34.4	11.5
40	11.5	23.5(D_2)	157	3.0	19.9	6.6
41	11.4	23.7	157	3.0	32.3	10.8
42	11.5	46.2	157	8.0	17.5	2.2

TABLE IV

FRACTIONATION OF HYDROCARBON PRODUCTS

No.	+ΔH.C., cc.	CH_4, cc.	C_2H_6, cc.	C_3H_8, cc.
41	3.7	4.2		
42	2.0	2.2		
100	5.3	6.2	4.2	8.7

Kinetics.—The kinetic studies were made at three temperatures and are summarized in Table V. Figure 2 shows the comparative rates of the ethane and propane reactions. With propane as with ethane the rate of decomposition increases slightly with time. Analysis of the rate measurements indicates a reaction strongly inhibited by hydrogen and weakly by hydrocarbon products, the numerical data yielding the values presented in

TABLE V

KINETICS OF HYDROGENATION DECOMPOSITION OF PROPANE

No.	C_3H_8, cc.	H_2, cc.	Temp., °C.	Time, hrs.	+ΔH.C., %	Conversion % per hr.
87	23.2	47.0	138	23.0	6.8	0.30
88	11.5	35.4	138	13.2	8.8	.67
89	11.5	23.2	138	5.0	10.2	2.04
90	17.4	35.3	138	14.0	8.9	0.63
83	23.0	46.8	157	5.0	12.1	2.4
84	23.3	71.7	157	13.0	9.5	0.73
85	11.4	23.3	157	1.1	13.1	11.9
86	11.3	53.2	157	5.0	9.2	1.8
91	22.9 + 25.0 (CH_4)	46.4	157	7.0	13.6	1.9
93	22.8 + 23.0 (C_2H_6)	46.0	157	7.4	8.5	1.2
92a	23.1	46.3	172	0–1.1	14.5	13.2
b				–3.8	43.1	11.3
c				–6.8	87.8	12.9
94	23.0	69.6	172	3	13.5	4.5
95	22.9	46.4	172	1	13.6	13.6
96	11.5	46.3	172	1	14.3	14.3
100	13.8	28.0	172	1	38.5	38.5

Table VI. From the temperature coefficient of the process we deduce an activation energy of ~34 kcal.

TABLE VI

KINETICS OF HYDROGENATION DECOMPOSITION

$k \propto (C_3H_8)^x(H_2)^y(C_2H_6)^z(CH_4)^w$

Temp., °C	x	y	z	w
138	+0.91	−2.70	....	....
157	+ .94	−2.43	−0.24	−0.07
172	+ .90	−2.66	....	....

On the average, $k \propto (C_3H_8)^{+0.92}\ (H_2)^{-2.6}$

The Exchange Reaction of Propane and Deuterium: (a) Equilibrium.—The catalyst was washed first with $2H_2 + 1D_2$ and then experiments were made with $C_3H_8 + 2D_2$ mixtures. Before Expts. 64 and 65 the wash gas was $1H_2 + 1D_2$, and before Expt. 74 the wash gas was pure D_2. The data are presented in Table VII.

TABLE VII

EQUILIBRIUM OF EXCHANGE REACTION

No.	C_3H_8, cc.	D_2 cc.	Temp., °C.	Time, hrs.	% D in H_xD_y	% C–D in $C_3H_xD_y$	$K = \frac{CD}{CH} \times \frac{H}{D}$
68	11.6	23.4	65	10.3		39.8	
69	11.6	23.5	65	3.0		20.9	
48	11.6	24.1	80	6.0		36.8	
49	11.7	24.1	80	13.0		39.3	
73	11.6	23.5	80	11.0	24.7	45.6	2.57
50	11.7	23.7	98	3.8	21.8	39.4	2.33
62	11.6	23.5	98	4.2	23.3	41.2	2.31
63	11.5	22.6	98	5.2	22.5	40.9	2.38
65	11.6	45.6	98	1.1		44.8	
64	11.5	45.6	98	5.1	40.2	61.0	2.32
46	11.6	23.7	110	1.1		40.4	
47	11.6	23.6	110	3.0		38.6	

In addition to the hydrocarbon exchange in this system there is, as pointed out in an earlier section, another source of exchange, namely, the kieselguhr support. Therefore, the hydrocarbon concentrations of equilibrium mixtures depend on the previous history of treatment of the catalyst. Exact equilibrium constants require, therefore, analysis of *both* hydrogen and hydrocarbon contents of the equilibrium mixture. In the experiments for which these analyses are available satisfactory constants are obtained with mean values, $K_{98} = 2.34$ and $K_{80} = 2.57$. From these we deduce a heat of reaction of 1.4 kcal.

(b) Kinetics.—In the kinetic experiments the catalyst was washed with deuterium before each run. The initial condition of the catalyst was therefore identical in all runs. The variation in the C–D percentage is undoubtedly the better way to measure the rate of reaction because, as the last column in Table VIII shows, lower values of exchange in the hydrogen occur due to the existence of the water–deuterium exchange.

TABLE VIII

No.	C_3H_8, cc.	D_2, cc.	Temp., °C.	Time, hrs.	% D in H_xD_y	% CD in $C_2H_xD_y$	% C–D per hr.	H exchanged, cc.	C–D exchanged, cc.
79	11.3	22.7	21.5	7.0	78.1	13.4	0.19	9.5	12.1
74	11.5	45.8	65	2.0	85.8	13.0	6.5	12.1	12.0
75	11.4	22.9	65	1.0	81.0	11.1	11.1	8.3	10.1
76	22.8	46.0	65	2.0	80.7	10.0	5.0	16.9	18.2
77	11.4	11.5	65	0.5	.	9.6	19.2	.	8.7
78	11.5	23.6	65	1.0	82.4	10.4	10.4	7.8	9.6
69	11.6	23.5	65	3.0	.	20.9	7.0	.	19.4
70	11.6	23.6	80	1.0	.	24.5	24.5	.	22.7
71	11.6	55.0	80	2.0	.	27.0	13.5	.	25.1
80	11.4	22.8	80	0.5	73.6	17.2	34.4	11.6	15.7

The exchange reaction with propane occurs at temperatures ~40° lower than that with ethane.

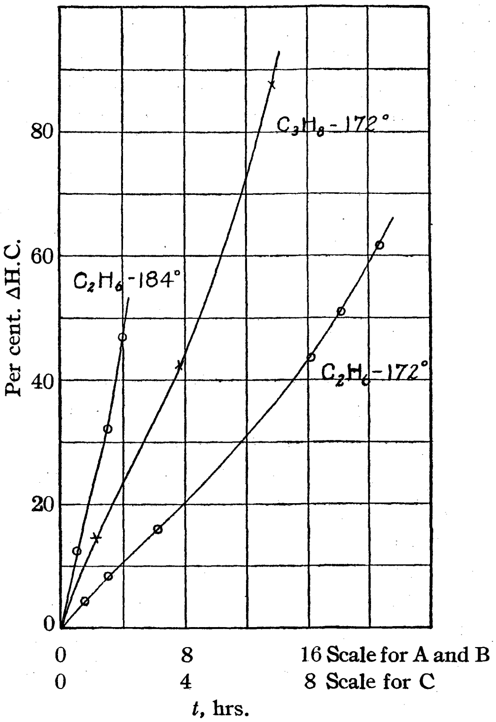

Fig. 2.

The activation energy of the process, ~19 kcal., is again much smaller than the value of ~34 kcal. found for the hydrogenation decomposition process. The inhibiting effect of hydrogen is also much less marked than in the decomposition process, the kinetics following the equation, $k \propto (C_3H_8)^{0.62}\ (D_2)^{-0.76}$, in contrast to $(H_2)^{-2.6}$ in the decomposition reaction. We refer to this point later.

Preparation of Propane-*d*$_8$.—The previous data suggested the following method of preparation of C_3D_6. A mixture of 22.6 cc. of C_3H_8 and 45 cc. of D_2 was left in contact with the nickel catalyst for three hours at 98° and then the equilibrated propane was separated in a liquid air trap. The propane thus recovered was subjected to six further successive treatments with deuterium under similar conditions. In the sixth conversion the deuterium recovered was 95% D. In the seventh it was 97.5% D. From the equilibrium constant $K_{98°} = 2.34$ this value corresponds to a propane of C–D content 98.9%. The product was fractionated under reduced pressure to remove a trace of ethane-d_6. The gas was then analyzed in the thermal conductivity gage. The properties of this preparation will be described elsewhere.

Hydrogenation of Ethylene.—The interaction of hydrogen and ethylene on the nickel catalyst under the conditions specified in Table IX showed no breaking of the carbon–carbon bond up to a temperature of 138° and was the straight hydrogenation.

TABLE IX

No.	C_2H_4, cc.	H_2, cc.	Temp., °C.	Gas recovered, cc.	H.C. (C_2H_6), cc.
24	18.5	37.4	20	38.0	18.4
25	18.9	38.7	80	38.7	18.9
101	19.9	44.2	138	44.2	20.1

Experiments with deuterium are recorded in Table X. The catalyst was again that used in the experiments of Table I. Experiment 82 is not comparable with Experiments 107–112 in which latter group the activity of the catalyst was changed due to a previous heat treatment. The comparison experiments were with a copper catalyst obtained by alternate reduction and oxidation of copper oxide granules (1.5 g.) with a final reduction and evacuation at 270°. The catalysts were in all cases well washed with deuterium.

TABLE X

REACTION OF ETHYLENE AND PROPYLENE WITH D_2 ON Ni AND Cu CATALYST

No.	Catalyst	C_2H_4, cc.	D_2, cc.	Temp., °C.	% D in H_xD_y	% C–D in H.C.	C–D exchanged, cc.	% exchange in C–H of C_2H_4
81	Ni	19.7	47.6	20	91.4	35.7	3.3	4.3
112	Ni	19.8	38.9	−80	97.1	33.4	0.6	0.8
107	Ni	19.5	39.7	−24	89.8	36.7	4.4	5.8
108	Ni	19.5	41.4	65	82.8	39.7	8.0	10.3
113	Cu	19.4	38.5	0	91.8	35.1	2.6	3.4
		C_3H_6						
115	Cu	19.0	40.4	0	83.8	28.5	6.5	5.7

On nickel the rate of hydrogenation was very rapid throughout the whole temperature range studied, −80 to 65°. Reaction at each temperature was complete within fifteen minutes. On the copper catalyst about one hour and a half was required at 0°. On this catalyst the amounts of hydrogen and saturated hydrocarbon adsorbed are very small and the catalytic hydrogenation can be used for analytical determinations of ethylene and propylene in gaseous mixtures.[6]

If no exchange reaction occurred between ethylene and deuterium the C–D concentration in the ethane obtained would be 32.9 and 24.2% if propylene were converted to $C_3H_6D_2$ since the deuterium content of the gas used was 98.7% D. Excess C–D percentages in the product indicate exchange.[8] The eighth column of Table X shows the results of calculations of exchange on this basis, expressed as cc. of C–D bonds, to be compared with the amount of hydrogenation, expressed also as cc. of C–D bonds, in each experiment approximately 39 cc. It will be observed that the C–D bonds produced by exchange increase with the temperature, that the activation energy of exchange is higher than that of hydrogenation and that the former is slower than the latter throughout our temperature range. These conclusions are different from those reached by Farkas, Farkas and Rideal.[9]

The copper catalyst becomes, consequently, a most convenient contact agent on which to prepare partially exchanged ethanes and propanes of known deuterium content from controlled mixtures of ethylene or propylene and deuterium, since the amounts of residual adsorption of hydrogen and hydrocarbon on copper after evacuation are negligibly small and exercise no measurable effect on the composition of the mixture introduced.

Polymerization of Ethylene.—The nickel catalyst used in the preceding experiments was evacuated for one and a half hours at 340°, 19.9 cc. of ethylene was introduced at 23° and left in contact for thirteen hours. The amount of permanent gas ($H_2 + CH_4$) produced was negligible. The gas recovered by freezing-out in a liquid air trap had a volume of 11.5 cc. This recovered gas was fractionated under a reduced pressure and found to contain 8.8 cc. of a C_2-fraction, a negli-

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(8) Wheeler and Pease [THIS JOURNAL, **58**, 1665 (1936)] found no exchange.

(9) Farkas, Farkas and Rideal, *Proc. Roy. Soc.* (London), **A146**, 630 (1934).

gible amount of C_3-fraction and 2.7 cc. of a C_4- or higher fraction. By hydrogenation with the copper catalyst the C_2-fraction proved to be 86% ethylene and 14% ethane. The higher fraction was hydrogenated to methane at 300° on nickel and the average number of carbon atoms in the molecule was found to be 4.17.

The gas left on the original catalyst after the liquid-air removal process was converted on the catalyst to methane with hydrogen at 300°. Methane to the extent of 9.6 cc. was thereby produced.

From these data we can calculate the following carbon balance of the polymerization process: H_2, CH_4, C_3H_6 and C_3H_8 are produced in negligible amounts; 38% C_2H_4 was recovered unchanged; in addition 6.3% C_2H_6 and 29% (and C_4H_{10}?) with some higher hydrocarbons were formed. The residue on the catalyst amounting to 24% was recoverable as methane by hydrogenation, leaving 3% of the carbon not accounted for in the analysis. This result shows that ethylene certainly polymerizes on a nickel catalyst at room temperatures and that the reactions with hydrogen present must be quite complex, involving hydrogenation, exchange, polymerization and, at sufficiently high temperatures, a decomposition process. It is thus much more complex than the ethane case. The absence of methane and propane indicates the remarkable stability of the C—C bond which does not materially break while these several processes of hydrogenation, exchange and polymerization are freely occurring.

Discussion of Results

As in the case of ethane[2] the apparent activation energy required to break the C–C bond in propane on the catalyst surface is higher than that required to break the C–H bond. Kinetic studies reveal, as in the case of ethane, that the inhibitory effect of hydrogen is much more marked in the case of C–C bond breaking than in the case of the C–H bond. The exchange reaction is proportional to the -0.76 power of the hydrogen concentration and the decomposition to the -2.6 power. In our present experiments we have studiously avoided experimental conditions in which carbon deposition might occur and the excellent constancy of activity of the catalyst throughout a long series of experiments is additional evidence that such carbon deposition has not occurred. We therefore can eliminate this possibility as the cause of the high inverse power effect of hydrogen from those discussed in Section II of this series. The form of the kinetic expression in both reactions indicates that the catalyst surface is largely occupied by hydrogen. The bare centers available for activated adsorption of propane should therefore be inversely proportional to some fractional power of the deuterium concentration. The data on the exchange reaction agree with this conclusion and indicate a fraction, -0.76. The much higher inhibitory effect in the decomposition reaction indicates quite decisively that much larger areas of surface are required for the propane to undergo this reaction than for the exchange process. At least two elementary spaces (in the sense of Langmuir) of a less frequent type than those adequate for exchange are demanded by an exponent of magnitude, -2.6. It is possible that even more than two elementary spaces are required for the dissociative adsorption which sunders the C–C bond. Whatever the area demanded, the kinetic studies here reported are excellent proof of the theory of active centers specific for a particular reaction even though the reactions studied are, as in this case, two different reactions with the same two gases present in the same concentrations. The range of temperatures in which the reactions could be studied was not sufficiently great for any variation in the dependence on the hydrogen pressure to be revealed. The abnormally high activation energy of the process may, however, as in the case of ethane, be explained as due to the composite effects of reaction temperature and relative surface coverage.

In the case of ethylene and propylene it is to be noted that exchange occurs even on a relatively inactive exchange catalyst such as copper, on which, under the conditions employed, no activation of the C–H or C–C bonds in saturated hydrocarbons occurs. We thus conclude that the presence of the double bond in the olefin markedly weakens the C–H bonds so that exchange occurs prior to hydrogenation, or at least during the hydrogenation process, possibly according to the suggested mechanism of Horiuti and Polanyi.[10]

General Discussion

From the data presented in the group of papers of which this is the third, we conclude that, under

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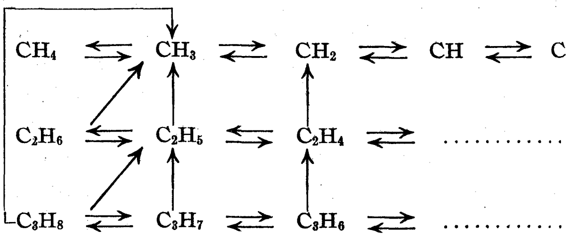
[10] Horiuti and Polanyi, *Trans Faraday Soc.*, **30**, 1171 (1934).

the conditions of our experimental work, the activated adsorption of saturated hydrocarbons is dissociative in type. We illustrate the various possibilities diagrammatically (the hydrogen atoms formed by dissociation being omitted for simplicity) thus



In respect to the positions of equilibria in such a complex system we observe that, with a high partial pressure of hydrogen, the equilibrium is largely on the molecular side and at low hydrogen partial pressure the equilibrium shifts toward carbon. The higher the hydrocarbon the more pronounced the shift toward the carbon side. In the absence of hydrogen, ethane changes to methane and carbon which are the only thermodynamically stable molecules in a system so constituted.[4] Below 300°, the equilibrium in the system $CH_4 \rightleftarrows C + 2H_2$ is pronouncedly on the methane side so that if the carbon is in a sufficiently active form it can be converted to methane with hydrogen.[4]

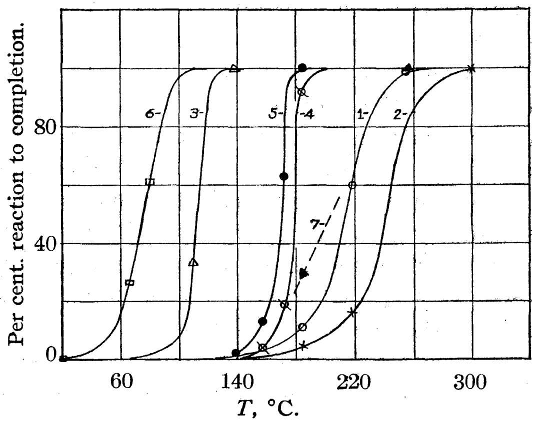


Fig. 3.—

Curve	Reaction	Time, hrs.
1	$CH_4 + CD_4 \rightarrow$ Ex.	1
2	$CH_4 + D_2 \rightarrow$ Ex.	1
3	$C_2H_6 + D_2 \rightarrow$ Ex.	2.5
4	$C_2H_6 + H_2 \rightarrow 2CH_4$	1
5	$C_3H_8 + 2H_2 \rightarrow 3CH_4$	1
6	$C_3H_8 + D_2 \rightarrow$ Ex.	1
7	$CH_4 + D_2O \rightarrow$ Ex.	11

With mixtures of methane and D_2O vapor, owing to the low H-atom concentration on the surface, the dissociative adsorption of methane will proceed markedly toward carbon. The deuteromethane which results will be formed not only from CH_3 fragments but also from CH_2 and CH fragments. We thus explain the abnormal distribution of the deuterium in the deuteromethanes produced by interaction with water[3] in contrast to the approximately equilibrium distribution when deuterium is used for the exchange process, methyl groups being the predominant fragments in this case.

The relatively strong adsorption of hydrogen and deuterium in comparison with the hydrocarbons explains the slowness of the $CH_4 + D_2$ exchange in comparison with the CH_4–CD_4 exchange.[3] With the higher hydrocarbons, two types of activation of the C–H and C–C bonds are involved. The activation of the former requires less apparent energy than that of the latter, is less adversely affected by hydrogen than is the latter. Our data reveal no evidence of the occurrence of reverse processes such as $2CH_2 = C_2H_4$, occurring from an upper to a lower level in the diagram given above. Under different conditions, as for example in the Fischer process of gasoline synthesis, such processes may be occurring.

We summarize, for comparative purposes in Fig. 3, the velocities of the various reactions we have studied on nickel catalysts. There are variations in the activities of the catalysts used, so that the data are only to be taken as approximate for comparison purposes. They do, however, reveal, the general course of activation as we proceed from methane toward the more complex hydrocarbons.

Summary

1. The exchange reaction between propane and deuterium on a nickel catalyst takes place in a lower temperature range, by ~90°, than that of the hydrogenation–decomposition to yield ethane and methane.

2. The kinetics of the two processes have been studied. The reactions are inhibited by hydrogen, the exchange to the −0.76 power, the decomposition to the −2.6 power of the hydrogen concentration.

3. Methods for the preparation of propane-d_8 as well as deuteropropanes and deuteroethanes of known C–D content have been described.

4. The availability of the hydrogen in a nickel–

kieselguhr catalyst for exchange reactions has been studied. Adsorbed hydrogen and adsorbed water vapor may be removed by evacuation at 218°. Other hydrogen sources of reproducible availability are held tenaciously in the kieselguhr, probably as bound water. These are difficult to remove even at 400–500°, and exchange with deuterium to increasing extents with increase of temperature.

5. The deuterium–ethylene reactions on nickel in the range −80 to 65° results in some exchange as well as the addition reaction. A copper catalyst also shows activity in exchange.

6. Ethylene polymerizes to C_4 and higher hydrocarbons at 0° on nickel, but the breaking of the C–C linkage is negligible.

7. A general discussion in terms of the dissociative adsorption of the saturated hydrocarbons has been given.

PRINCETON, N. J. RECEIVED JANUARY 7, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Aqueous Solubilities of the Isomeric Pentanols

BY P. M. GINNINGS AND RHODA BAUM

An important factor in most investigations of the relationship between molecular structure and aqueous solubility of organic compounds is the molecular weights of the compounds studied. In fact its domination frequently tends to obscure the effect of lesser factors. Evidently, limitation of a study to isomers should simplify considerably analysis of the results and for this reason, a study of the aqueous solubilities of the eight isomeric pentanols or amyl alcohols seemed worthwhile. Search of the literature revealed approximate solubilities for many of these isomers but apparently only two have been measured precisely. Butler[1] using an interferometric method measured the solubility of *n*-pentanol (*n*-butylcarbinol) at 25° as 2.208 weight percentage. Kablukov[2] using the volumetric method of Hill[3] determined the value for isobutylcarbinol (isoamyl alcohol) at a number of temperatures. Values for the latter are also given in the "International Critical Tables."[4]

The solubilities of these two compounds were also determined in the present paper as a check upon our experimental work and the results seem to agree within the accuracy of our method.

Results of our determination of the weight percentage solubilities of these eight isomers are given in the table. The difference between the larger weight percentage for a given temperature and isomer and one hundred represents the solubility of water in that particular isomer. Analysis of the data indicates that the one tertiary isomer is more soluble than any of the three secondary isomers and that these in turn are more soluble than any of the four primary isomers. The solubility increases as the hydroxyl group approaches the center of the molecule (Nos. 1, 5 and 6). If the analysis is limited to either the primary or secondary isomers, it is evident also that the solubility in water increases as the structure of the molecule becomes more compact. However, the most compact primary isomer (No. 4) is not as soluble as the least compact secondary isomer (No. 5). Usually the more soluble the alcohol in water, the more soluble the water is in the alcohol. Of interest also is the fact that as the temperature increases from 20 to 30°, the solubility of all eight isomers decreases.

Experimental

With one exception, the compounds used for the final determinations were prepared by purification of products synthesized by one of the Grignard reactions. *t*-Butylcarbinol was prepared in this Laboratory by the action of *t*-butylmagnesium chloride upon paraformaldehyde with the usual hydrolysis, etc. Dimethylethylcarbinol was prepared by the action of ethylmagnesium bromide upon acetone in the usual Grignard procedure. The other compounds were Eastman best grade of products. The isobutylcarbinol probably was obtained originally as a by-product from a fermentation process and was known to contain some of the active amyl isomer. Approximately seventy-five aqueous extractions, drying with anhydrous potassium carbonate and final fractional distillation over metallic calcium seemed to purify this satisfactorily.

In general, all products from the Grignard syntheses were fractionally distilled with a short column (reflux

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[1] Butler, Thompson and MacLennan, *J. Chem. Soc.*, 674 (1933).

[2] Kablukov and Malischeva, THIS JOURNAL, **47**, 1559 (1925).

[3] Hill, *ibid.*, **45**, 1145 (1923).

[4] "International Critical Tables," Vol. III, p. 388.

TABLE I

			Wt., % Alc.		d 25/4		d/4, liq. phases	
No.	Compound	Temp., C.			pure alc.	B. p. (760 mm.), °C.	Alc. rich	Water rich
1	*n*-Butylcarbinol	20	2.36	92.52	0.8110	137.6–138.3	0.8317	0.9939
		25	2.19	92.54			.8287	.9930
		30	2.03	92.35			.8253	.9919
2	Isobutylcarbinol	20	2.85	90.53	.8071	131.5–131.7	.8286	.9941
		25	2.67	90.39			.8257	.9932
		30	2.53	90.24			.8188	.9921
3	*s*-Butylcarbinol	20	3.18	91.05	.8106	128.4–129.1	.8311	.9943
		25	2.97	90.81			.8288	.9930
		30	2.83	90.74			.8239	.9928
4	*t*-Butylcarbinol	20	3.74	91.77	M. p.	113.0–114.0	.8243	.9936
		25	3.50	91.64	48–49°		.8216	.9930
		30	3.28	91.46			.8178	.9925
5	Methyl-*n*-propylcarbinol	20	4.86	88.30	0.8056	119.2–119.7	.8317	.9914
		25	4.46	88.21			.8280	.9909
		30	4.13	88.10			.8243	.9898
6	Diethylcarbinol	20	5.61	91.81	.8195	115.4–115.9	.8368	.9920
		25	5.15	91.68			.8330	.9914
		30	4.75	91.42			.8294	.9903
7	Methylisopropylcarbinol	20	6.07	88.12	.8134	111.1–111.9	.8390	.9909
		25	5.55	88.07			.8352	.9902
		30	5.10	87.95			.8348	.9879
8	Dimethylethylcarbinol	20	12.15	75.74	.8055	101.9–102.1	.8662	.9837
		25	11.00	76.53			.8552	.9829
		30	10.10	77.31			.8498	.9828

ratio about 7:1) off metallic calcium, using a precision thermometer, graduated in 0.1° with the range of 100–150°. Dimethylethylcarbinol was distilled off calcium oxide. All boiling points given in the table have been corrected to 760 mm. pressure using Craft's rule when the dT/dp was not known; stem correction was applied when needed.

Compounds 3, 5, 6, and 8 in the table were also obtained in the Technical grade of purity. These had as their origin the isomeric pentenes of petroleum and were quite difficult to purify completely. However, for purposes of comparison these four were purified as carefully as possible by fractional distillation through a 1-m. column, fractionally extracted with water, fractionally salted-out with potassium carbonate and again fractionally distilled through the 1-m. column. In all cases the middle fractions were taken and the extremes discarded. The solubilities of the products were then compared with those obtained on the compounds prepared by the Grignard syntheses and which are given in the table. Agreement was usually close except in the case of the dimethylethylcarbinol; the solubility of the product derived from the Technical was approximately 0.3 wt.% higher than the other at all three temperatures.

Hill's volumetric method mentioned previously in this article was used with some adaptations and refinements to measure the solubilities. A pair of two-bulb graduated and calibrated flasks was constructed mainly from portions of Babcock milk test bottles. The two constricted portions of each double-bulbed flask were made from the graduated necks and so were already graduated in intervals of 0.02 ml. This permitted measurement of the volumes of the liquid phases with an accuracy better than 0.01 ml.

The general procedure was to introduce known weights of the particular alcohol and distilled water (weighings accurate to better than 1 mg.) into the flask stoppered with an excellent grade cork stopper. Flask and contents were then shaken mechanically in a constant temperature water-bath, maintained thermostatically and manually to the desired temperature plus or minus 0.1°. Sufficient time was allowed for the liquids to reach equilibrium, the two liquid phases were allowed to separate and the total volume reading in the flask noted. The flask was then centrifuged in the usual Babcock centrifuge to sharpen the dividing line between the two liquid phases and then returned to the constant temperature bath. After the total volume reading had returned to the same as the original one noted, the reading of the line dividing the two phases was made. From these data, volumes of the two phases were calculated. Ratios of the volumes of the two sections of the two flasks were approximately 1:5 in one and 5:1 in the other. Total volume of each flask was approximately 65 ml. With the weights of the components in both flasks known and both pairs of volumes calculated, sufficient data were in hand to substitute in the pair of simultaneous equations to get the concentrations of each component in each phase. Subsequently, the weight percentages were calculated from the latter values as explained in detail by Hill.

The reliability of the method was better than 0.1 wt. % in practically all of the cases and the authors feel that the validity of the results will approach this limit. Increase of the limits to 0.2 wt.% should probably be allowed in the case of the dimethylethylcarbinol.

Summary

Aqueous solubilities of the eight isomeric pentanols have been determined for 20, 25 and 30°.

The one tertiary isomer is more soluble than any of the three secondary isomers which in turn are more soluble than any of the four primary isomers. The solubility increases as the hydroxyl group approaches the center of the molecule. Limitation of the comparisons to either the primary or the secondary group reveals that the more compact the molecular structure, the greater is the aqueous solubility. The solubility of all eight isomers decreases as the temperature increases from 20 to 30°.

GREENSBORO, N. C. RECEIVED APRIL 5, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY AND ST. JOHN'S UNIVERSITY]

Equimolar Condensations of Aldehydes with Phenols. The Preparation of Primary Saturated Alkylphenols[1]

BY JOSEPH B. NIEDERL, VICTOR NIEDERL, S. SHAPIRO[2] AND MARTIN E. MCGREAL

Condensation of carbonyl compounds (aldehydes and ketones) with multimolar quantities of a phenol usually results in the formation of the corresponding alkylidene-di-phenol.[3] Dianin and von Braun,[4] however, made the observation that saturated secondary or tertiary alkylphenols are obtained when the intermediate polymeric condensation products resulting from the action of hydrochloric acid upon a mixture consisting of several moles of a phenol and one mole of a ketone, aliphatic (di-*n*-propyl, methyl hexyl ketone and dichloroacetone) as well as aromatic ketones (acetophenone, ω-chloroacetophenone) are subjected to pyrolysis. The formation of saturated alkylphenols from ketone-phenol polymers was a rather unexpected observation and the expression "disproportionation" process was suggested by von Braun for this phenomenon.

In all of the above investigations multimolar quantities of phenol were used. It was the purpose of the research set forth in this communication to investigate equimolar condensations of saturated aliphatic aldehydes with phenols to establish experimentally the following: (a) whether it is possible to obtain mole for mole addition; (b) whether these additions take place analogous to the addition of halogen acids or hydrocyanic acid to the carbonyl bond, or whether the addition takes place as in aldol condensations; (c) to investigate the chemical nature of the intermediate polymer; and (d) to investigate the behavior of these aldehyde–phenol polymers upon pyrolysis, particularly as to the possibility whether a similar "disproportionation" could be observed in the aldehyde series as has already been established in isolated cases in the ketone and indane series.[5] Although the end-products, the saturated primary alkylphenols, could be identified easily, analysis of the intermediate polymeric condensation products did not lead to uniformly interpretable results. Some of these products, when reprecipitated, powdered and completely dried in a vacuum desiccator over phosphorus pentoxide for several months, gave results upon quantitative analysis which corresponded closely to polymeric alkylenephenols. The pyrolysis of the condensation products of phenols and the three cresols with the following aldehydes were studied.

Formaldehyde and phenol yielded a small amount of a cresol. Acetaldehyde and phenol (I) and the three cresols (II, III, IV) gave the corresponding ethylphenol and ethylcresols upon pyrolysis of the Claisen solution soluble polymeric condensation products. Substitution of vinyl acetate for acetaldehyde yielded similar polymers. Propionaldehyde (V), *n*- and isobutyraldehyde (VI, VII), *n*-valeric aldehyde (VIII) and *n*-heptaldehyde (IX) and phenol gave the respective alkylphenols. These primary saturated alkylphenols were purified by repeated fractional distillation, then analyzed and further characterized as crys-

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[1] Presented before the Division of Organic Chemistry at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] Several parts are taken from the thesis of S. Shapiro, presented to the Graduate School of New York University in partial fulfilment of the requirements for the degree of Master of Science.

[3] Schmidlin and Lang, *Ber.*, **43**, 2806 (1910); Claus and Trainer, *ibid.*, **19**, 3009 (1886); Moehlau and Koch, *ibid.*, **11**, 283 (1878); L. Claisen, *Ann.*, **237**, 261 (1887); Th. Zincke, *ibid.*, **363**, 255 (1908); E. K. Bolton, U. S. Patent 2,069,573 (1937); H. S. Rothrock, *ibid.*, 2,069,560 (1937).

[4] Dianin, *J. Russ. Phys.-Chem. Soc.*, **23**, 540 (1891); *Ber.*, **25**, 336 (1892); J. v. Braun, *Ann.*, **507**, 15 (1933).

[5] Niederl, Niederl and Reznek, THIS JOURNAL, **58**, 657 (1936); Weissberger, *Ber.*, **44**, 1438 (1911); Weger and Billmann, *ibid.*, **36**, 644 (1903); Kramer and Spilker, *ibid.*, **29**, 561 (1896); **33**, 2260 (1900); **23**, 3278 (1890); Moschner, *ibid.*, **33**, 737 (1900); Stoermer and Boes, *ibid.*, **33**, 3016 (1900).

TABLE I

No.	Phenol; HAc deriv.	Formulas	B. p., °C. 760 mm.	M. p., °C.	$n^{25}D$	Sp. gr.^{20}	Phenol coeff.	Analyses, % Calcd. C	H	N. E.	Found C	H	N. E.
I	*p*-Ethyl-	$C_8H_{10}O$	210–212		1.5239	1.0123	10	78.69	8.19		78.51	8.04	
	HAc deriv.	$C_{10}H_{12}O_3$		90				66.67	6.67		66.60	6.28	180
II	2-Methyl-4-ethyl-	$C_9H_{12}O$	223–228		1.5372	0.9944	11	79.41	8.82		79.75	8.62	
	HAc	$C_{11}H_{14}O_3$		125				68.04	7.26	194	68.23	7.05	195
III	3-Methyl-4-ethyl-	$C_9H_{12}O$	230–235		1.5362	.9956	10	79.41	8.82		79.52	8.70	
	HAc	$C_{11}H_{14}O_3$		131				68.04	7.26	194	68.15	7.09	193
IV	4-Methyl-2-ethyl-	$C_9H_{12}O$	215–221		1.5340	.9949	10	79.41	8.82		79.63	8.98	
	HAc	$C_{11}H_{14}O_3$		133				68.04	7.26	194	68.05	7.10	195
V	*p*-*n*-Propyl-	$C_9H_{12}O$	228–230		1.5379	.999	14	79.41	8.82		79.16	8.47	
	HAc deriv.	$C_{11}H_{14}O_3$		86				68.04	7.26	194	67.91	7.45	196
VI	*p*-*n*-Butyl-	$C_{10}H_{14}O$	238–242		1.4981	.9664	21	80.00	9.33		79.67	9.12	
	HAc deriv.	$C_{12}H_{16}O_3$		81				69.23	7.69	208	69.07	7.69	207
VII	*p*-Isobutyl-	$C_{10}H_{14}O$	235–239		1.5319	.9796	18	80.00	9.33		80.24	9.61	
	HAc deriv.	$C_{12}H_{16}O_3$		124–125				69.23	7.69	208	69.02	7.42	205
VIII	*p*-*n*-Amyl-	$C_{11}H_{16}O$	248–253		1.5272	.9621	20	80.36	9.76		80.69	9.35	
	HAc deriv.	$C_{13}H_{18}O_3$		90				69.95	8.52	222	70.16	8.25	225
IX	*p*-*n*-Heptyl-	$C_{13}H_{20}O$	271–278		1.5090	.9583	21	80.83	10.88		80.51	10.46	
	HAc deriv.	$C_{15}H_{22}O_3$		94				72.00	8.80	250	71.92	8.79	251

talline aryloxy-acetic acids, prepared according to Shriner and Fuson.[6]

Experimental

_p_-Ethylphenol, _p_-Ethyl-_o_-cresol, _p_-Ethyl-_m_-cresol, _o_-Ethyl-_p_-cresol.—Molar mixtures of phenol or cresol and acetaldehyde were placed in a 2-liter 3-necked round-bottomed flask provided with a reflux condenser, a thermometer and a gas inlet tube extending to the bottom of the vessel. Two hundred cc. of glacial acetic acid was added and the reaction mixture cooled to about −5° by immersing the flask in an ice–salt mixture. A vigorous stream of dry hydrochloric acid gas was passed through the system for two hours and then the condensation product, a dark red oil, was poured into a large volume of cold water. A yellowish white precipitate formed which was washed repeatedly with cold and hot water, then filtered and dried; yield, almost quantitative. The thoroughly dry product was powdered, placed in a 250-cc. distilling flask and distilled under atmospheric pressure. The distillate, consisting of water, the respective phenol or cresol and the alkylated ethylphenol or ethyl cresol was taken up in ethyl acetate, this solution dried over calcium chloride and filtered. The solvent was distilled off and the residue fractionally distilled under atmospheric pressure. The lower boiling portion (about 30%) consisted mostly of the original phenol or cresol; the higher boiling portion (about 40%) was redistilled and consisted of the respective ethylphenol or ethylcresol. A charred residue (about 20%) remained in the distilling flask after pyrolysis.

Aryloxyacetic Acid (HAc Deriv.).—By the method of Shriner and Fuson, 1 g. of *p*-ethylphenol was dissolved in 5 cc. of a 33% sodium hydroxide solution and 1.5 g. of chloroacetic acid added. The mixture was shaken thoroughly and heated on a water-bath at 100° for one hour. The solution was then diluted with 15 cc. of water, acidified with dilute hydrochloric acid to congo red and extracted with 50 cc. of ether. The ether was washed with an equal volume of water and then shaken out with 25 cc. of a 5% sodium carbonate solution. This solution was acidified with dilute hydrochloric acid and the *p*-ethylphenoxyacetic acid which precipitated out filtered and dried on porous tile. It was recrystallized from diisobutylene. The cresoxyacetic acids were prepared in the same manner.

_p_-_n_-Propylphenol, _p_-_n_-Butylphenol, _p_-Isobutylphenol, _p_-_n_-Amylphenol, _p_-_n_-Heptylphenol.—These compounds were prepared in a similar manner as described above, except that the reaction was carried out at room temperature and condensation was complete in two and one-half to three hours. The temperature inside the reaction vessel rose to 60 to 80° and diminishing temperature indicated completion of the reaction. The condensation product was then poured into cold water and a heavy oil separated out which was taken up in ethyl acetate. This solution was washed exhaustively with water, then dried and distilled under atmospheric pressure. The distillate, consisting of water, phenol and the corresponding alkylated phenol, was again taken up in ethyl acetate, dried and fractionally distilled under reduced pressure. The higher boiling fraction, representing the respective alkylated phenol, was purified by redistillation. The yield ranged from 20 to 40%.

The acetic acid derivatives were prepared as described above, except that wherever the final precipitate was an oil it was extracted from the aqueous solution with ether, the ether permitted to evaporate at room temperature, whereupon the acetic acid derivative crystallized. All the derivatives were recrystallized from diisobutylene.

The phenol coefficients given are the average of six tests, performed in 30% alcoholic solution with *staphylococcus aureus* at 37°. The authors are indebted to Dr. Wm. A. Feirer of the Mulford Biological Laboratories, Glenolden, Pa., for performing these tests. The authors are further indebted to the Lambert Pharmacal Co., St. Louis,

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[6] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1935, p. 148.

Mo., for a research grant for the completion of this investigation.

Summary

Equimolar condensations of monohydroxyphenols with saturated aliphatic aldehydes were studied. It was found that polymers result in quantitative yields. Upon slow pyrolysis, these polymers yield the corresponding saturated primary alkylphenols. These types of condensations are being extended to unsaturated and aromatic aldehydes, reducing saccharides as well as to ketones, particularly cyclic ketones (cyclopentanone, cyclohexanone, alkyl cyclohexanones and camphor).

NEW YORK, N. Y. RECEIVED MARCH 4, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN COMPANY]

Some Derivatives of Ortho-Hydroxyphenylmercuric Chloride

BY HANS P. ANDERSEN AND MERRILL C. HART

In earlier reports it has been shown that variations in structure have a limited influence on bacteriostatic properties of organic mercury compounds,[1] and that more complex structures were not as effective as mercury derivatives of hydrocarbons or phenols with limited substituents.[2] One very effective mercurial was found to be *o*-hydroxyphenylmercuric chloride, this compound also being bactericidal at some dilutions.[2] It seemed that possible derivatives of this compound could be prepared which would have similar properties.

Some imide derivatives of phenylmercuric nitrate have been described as being used in germicidal detergent or cosmetic compositions.[3]

In the present work some imide derivatives of *o*-hydroxyphenylmercuric chloride have been prepared and their bacteriological properties evaluated.[4] One has been found to be equally as good as the parent compound. It was found that, in general, imide derivatives were readily formed in alkaline solution, especially if the imide contained a carbonyl group. An attempt was made to prepare derivatives of pyrrole, auramine, carbazole and piperidine but only in the case of piperidine was a product obtained in the form of the hydrochloride. This was formed in the absence of alkali.

Although the simplest structures are most effective, it was thought that fatty acid derivatives might facilitate the *in vivo* activity by increasing diffusion into the surfaces in contact with the antiseptic. A few representative phenolmercuric fatty acid compounds have been prepared and described.

The table gives the results obtained together with melting points and analytical data.

TABLE I

Compound with $HOC_6H_4HgCl(o\text{-})$	Yield, %	M. p., °C.	Mercury analyses, % Calcd.	Found	Inhibiting dilution to *Staph. aureus* in 5 min.
Succinimide	72.3	232–235	51.1	50.8	1–75,000[a,b]
Saccharine	53.7	242–243	42.5	42.1	1–10,000
Phthalimide	96.3	223–224	45.5	45.6	1–20,000
Piperidine	79.3	126	48.3[c]	47.8	1–30,000
Theobromine	51	145–165	40.8[d]	40.3	1–10,000
Barbituric acid	48	...	56.1	56.3	1–20,000
Acetic acid	...	150–151	56.8	56.7	1–40,000
Pelargonic acid	60.7	135	44.4	44.1	1–20,000
Oleic acid	64.3	95–96	34.8	34.98	1–20,000
Lauric acid	74	135.5–136.5	40.6	40.3	1–20,000
Myristic acid	72	135–136[e]	38.5	38.3	1–10,000
Palmitic acid	90	129–131	36.5	36.3	1–10,000
Stearic acid	70	135–137[e]	34.7	34.4	1–10,000

[a] This compound was bactericidal 1–1000. [b] Phenol control 1–80. [c] This is the mercury content of the hydrochloride. Calcd. for $C_{11}H_{15}OHgHCl$: Cl, 8.81. Found: Cl, 8.41. [d] Monohydrate. [e] Mixed melting points with pelargonic and lauric acid derivatives were depressed.

Experimental

***o*-Hydroxyphenylmercuric Succinimide.**—Three and three-tenths grams of succinimide in 18.7 cc. of water, was added to 10.95 g. of *o*-hydroxyphenylmercuric chloride in 25 cc. of warm alcohol. This was cooled as much as possible without forming a precipitate and then 18.7 cc. of 10% potassium hydroxide was added. After shaking and further cooling, 11 g. of crude product was obtained melting at 222°. This was recrystallized from 200 cc. of alcohol and 100 cc. of water to give a final yield of 72.3%. The melting point was 232–235°.

The other imide derivatives were made in the same manner using either water or alcohol, depending on which was the better solvent for carrying out the reaction.

***o*-Hydroxyphenylmercuric Piperidine Hydrochloride.**—Five cubic centimeters of piperidine was added to 16.4 g.

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(1) Hart and Andersen, THIS JOURNAL, **56**, 2752 (1934).

(2) Hart and Andersen, *ibid.*, **57**, 1059 (1935). See also Phatak and Leake, *J. Pharmacol.*, **56**, 265 (1936).

(3) British Patent 432,689, July 31, 1935.

(4) We are indebted to Mr. E. A. Gibson, Bacteriological Laboratory, for these results.

of *o*-hydroxyphenylmercuric chloride in 25 cc. of alcohol. The product melted at 126°; yield 79.3%. The analytical data indicate that the hydrochloride is formed and that treatment with potassium hydroxide gives an *o*-hydroxyphenylmercuric hydroxide derivative. It is not stable to acetic acid, probably forming *o*-hydroxyphenylmercuric acetate.

***o*-Hydroxyphenylmercuric Hydroxide.**—Ten grams of *o*-hydroxyphenylmercuric chloride in 25 cc. of alcohol was treated with 17 cc. of 10% alcoholic potassium hydroxide, warming slightly and stirring vigorously. The product is insoluble.

Anal. Calcd. for $C_6H_6O_2Hg$: Hg, 64.5. Found: Hg, 64.7.

***o*-Hydroxyphenylmercuric Fatty Acid Compounds.**—The calculated quantity of *o*-hydroxyphenylmercuric hydroxide was suspended in warm alcohol and the fatty acid added and stirred with warming until solution resulted. On cooling the fatty acid derivative precipitated. It was recrystallized from alcohol and dissolved in dilute alcohol or alkaline solution for bacteriological study.

Summary

A number of imide derivatives of *o*-hydroxyphenylmercuric chloride have been prepared, one of which has bacteriostatic properties similar to the parent compound.

Some fatty acid compounds with *o*-hydroxyphenylmercuric hydroxide have been made which may promise to give enhanced *in vivo* activity.

KALAMAZOO, MICH. RECEIVED APRIL 21, 1937

[CONTRIBUTION FROM THE DEPARTMENTS OF BIOCHEMISTRY AND CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

The Identification of the Amino Acids: *p*-Toluenesulfonyl[1] Chloride as a Reagent

BY EVAN W. MCCHESNEY AND WM. KIRK SWANN, JR.

I. Introduction

Numerous reagents have been employed for the identification of the amino acids. Among these perhaps the most important group are those reagents which conjugate readily with the amino group, such as benzoyl chloride, β-naphthalenesulfonyl chloride, benzenesulfonyl chloride, *p*-nitrobenzoyl chloride, and phenyl isocyanate. With the passing of years, however, and the discovery of new amino acids, there have come to be gaps in our knowledge such that the derivatives of all of the known amino acids with any one of these reagents do not seem to have been described. Also, in some cases, the derivatives have been prepared, but it has not been possible to crystallize them. The result of this situation is that an investigator who has at hand a small amount of an unknown amino acid cannot rely safely on one derivative for the identification, since it may not crystallize, or it may not have been described. The object of this work has been to find, if possible, one derivative which would be satisfactory for all of the amino acids, and to describe it for those which are at present recognized as products of protein hydrolysis and are commercially available.

For this work two reagents not extensively used thus far in amino acid work were selected for study: *p*-toluenesulfonyl chloride and *p*-bromobenzenesulfonyl chloride. It was soon found that the derivatives obtained with the former crystallized much more readily; therefore it was selected to complete the study. The idea of using *p*-toluenesulfonyl chloride as a reagent for the amino acids is not a new one, Oseki[2] having prepared about a dozen of the compounds, and several other investigators having prepared one or more of them (see references to Table I). A considerable number of the amino acids have not been included in these studies, however, and in some cases there are serious discrepancies in the melting points recorded (see, for example, *d*-alanine, *d*-valine, and *l*-leucine in Table I). It therefore seemed worth while to try to repeat all of the work previously done and, if possible, to complete the list.

II. Materials.—The amino acids used in this work were the highest grade products of the Eastman Kodak Co., the Pfanstiehl Chemical Co., and Hoffman-La Roche, Inc., except those which are commonly prepared in the laboratory (glycine, *d,l*-alanine, *l*-tyrosine, *l*-cystine, and *d*-glutamic acid). The latter were prepared by the standard methods, crystallized from the appropriate solvents, and their purity was demonstrated by nitrogen analyses. The *p*-toluenesulfonyl chloride was an Eastman product, m. p. 67-69° (m. p. in the literature is 69°[3]).

III. Method.—The method used[4] is such a familiar one that it requires little comment. The amino acid, 0.01 equivalent as to combining power, is dissolved in 20 cc. of *N* sodium hydroxide, an ethereal solution of 2 g.

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[1] Presented at the Chapel Hill meeting of the American Chemical Society, April 14, 1937.

[2] Oseki, *J. Tokyo Chem. Soc.*, **41**, 8 (1920).

[3] *Cf.* Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. XI, p. 103.

[4] Fischer and Bergell, *Ber.*, **35**, 3779 (1902).

(0.01 mole) of *p*-toluenesulfonyl chloride is added, and the mixture is shaken mechanically for three to four hours. The ethereal solution is then separated off and the aqueous solution is acidified to congo red with hydrochloric acid. The derivative begins to crystallize at once (or separates as an oil which, on standing in the refrigerator, will eventually crystallize except in special cases to be discussed later). The crystals are collected on a filter and are recrystallized from a very small amount, usually 5 cc. or less, of 60% alcohol. The yield at this point is about 50% of the theoretical. Two or three crystallizations give a constant melting point.

Exceptions.—In the case of phenylalanine and tyrosine, the sodium salt of the derivative is sparingly soluble in water and separates out during the reaction. The semi-emulsion which results is acidified to congo red, whereupon the sodium salt goes into solution and the mixture separates into two layers. The derivative passes into the ethereal layer from which it begins to crystallize spontaneously in a few minutes; it may be collected on a filter. With these amino acids the yield is nearly quantitative and more of the solvent, up to 25 cc., is needed for crystallization. There is a second exception in the dicarboxylic acids, the derivatives of which are very soluble in water, therefore do not precipitate on acidification. They are converted to their dibutyl esters by the method of Gurin and Clarke[5] as described later.

IV. Experimental Data

The amino acid derivatives which could be crystallized were dried *in vacuo* over boiling ethyl alcohol in a drying pistol. They were analyzed for nitrogen by a semi-micro Kjeldahl method in order to demonstrate their purity; in the cases of cystine and methionine, sulfur was also determined, the Parr bomb method being used. The data are shown in Table I, which includes derivatives reported by other investigators to crystallize, but found in this work, however, to form persistent oils.

The *p*-toluenesulfonyl derivatives of the amino acids formed colorless crystals which usually separated in the form of needles or rods. The only important exceptions were the derivatives obtained from cystine and histidine; the former crystallized in the form of prisms of a gritty character, while the latter crystallized as rosets of needles. Of the various solvents used for recrystallization, only 60% alcohol seemed suitable for all of the derivatives. A few (notably those from glycine and alanine) crystallize from water, a few crystallize from benzene (only those from leucine and phenylalanine were tried), and a large number crystallize from β,β'-dichloroethyl ether (those from cystine, serine and histidine were the only exceptions found). However, the question of solubility has been studied extensively by others, notably Oseki, and no discussion seems called for in this paper.

In addition to the melting points, further evidence as to the nature of the compounds is obtained readily by analyzing for nitrogen or sulfur, or by titrating the carboxyl group in alcoholic solution, using phenolphthalein as an indicator. This gives results which agree exactly with the nitrogen determinations.

TABLE I

DATA ON THE *p*-TOLUENESULFONYL DERIVATIVES OF SOME AMINO ACIDS

Amino acid	Melting point of derivative, °C. In literature	Melting point of derivative, °C. Found (uncorr.)	N, % Calcd.	N, % Found
d,l-Alanine	138–139[6]	138–139	5.76	5.79
d-Alanine	92– 94[2] 131–132[6]	132–133	5.76	5.62
l-Aspartic acid	126–128[2] 139–140[7]	Oil		
l-Cystine (di-subs.)	204–205[2]	201–203 (dec.)	5.11	5.08
d-Glutamic acid	115–117[8]	Oil		
Glycine	146[2] 147[9] 149–150[10]	147	6.11	6.04
l-Histidine		202–204 (dec.)	13.59	13.45
l-Hydroxyproline[11]		153	4.91	4.97
d,l-Isoleucine	141 (corr.)[12]	139–140	4.91	4.86
d-Isoleucine		130–132	4.91	4.83
l-Leucine	111.5[2] 113.5[13] 124 (corr.)[14]	121–122	4.91	4.91
d,l-Methionine		104–105	4.62	4.78
d,l-Norleucine		124	4.91	4.88
d,l-Phenylalanine	134–135[15]	134–135	4.39	4.40
l-Phenylalanine	164–165 (corr.)[16]	161	4.39	4.36
l-Proline	130–133[17]	Oil		
d,l-Serine[11]		212–213 (dec.)	5.41	5.25
l-Tryptophane	176[2]	Oil		
l-Tyrosine (di-subs.)	117–119[2,18]	113–114	2.86	2.84
d-Valine	110–111[2] 147[19]	147	5.17	5.08

Sulfur analyses: For di-*p*-toluenesulfonyl-*l*-cystine calcd., 23.35%; found, 23.58%. For *p*-toluenesulfonyl-*d,l*-methionine, calcd., 21.14%; found, 21.36%.

V. Treatment of Non-Crystalline Derivatives.—The derivatives of glutamic and aspartic acids, arginine, lysine, tryptophane and proline were found not to crystallize. The same experience was reported by Oseki as regards arginine and lysine, but the other four derivatives have been crystallized by various investigators. In this work, for lack of material, tryptophane was not studied further; the preparation of a crystalline derivative from it would be of little practical value, however, since it is readily recognized by other means. The other derivatives were taken up in butyl alcohol if they precipitated as oils, or were extracted from aqueous solution by butyl alcohol if they did not precipitate. They were then converted

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(5) Gurin and Clarke, *J. Biol. Chem.*, **107**, 403 (1934).

(6) Gibson and Simonsen, *J. Chem. Soc.*, **107**, 799–802 (1915).

(7) Freudenberg and Noe, *Ber.*, **58B**, 2407 (1925).

(8) Bergell, *Z. physiol. Chem.*, **104**, 185 (1919).

(9) Wallin, Dissertation, *Acta Universitatis Lundensis*, **28**, 3 (1892).

(10) Fischer and Bergmann, *Ann.*, **398**, 117 (1913).

(11) Enough reagent was used to give the disubstituted derivative, but only the monosubstituted derivative was obtained. It is therefore undoubtedly the N-derivative.

(12) Bouveault and Locquin, *Compt. rend.*, **141**, 116 (1905).

(13) Karrer and Kehl, *Helv. Chim. Acta*, **13**, 57 (1930).

(14) Fischer and Lipschutz, *Ber.*, **48**, 365 (1915).

(15) In Oseki's work it apparently is not stated what form of the amino acid he had in hand. Hence except in this one case it has been assumed that he used the naturally occurring form. Here the coincidence of melting points would seem to indicate that he used the racemic substance. Translation of Oseki's work was by Dr. A. R. Merz.

(16) Ref. 14, p. 374.

(17) Kapfhammer and Eck, *Z. physiol. Chem.*, **170**, 306 (1927).

(18) The N-*p*-toluenesulfonyl derivative has been described by Fischer and Lipschutz, ref. 14, p. 376. M. p. 187–188°C. The derivative reported here is N,O-di-*p*-toluenesulfonyl-*l*-tyrosine.

(19) Karrer and van der Sluys Veer, *Helv. Chim. Acta*, **15**, 750 (1932).

to their butyl esters by the method of Gurin and Clarke.[5,20] After evaporation of the butyl alcohol as directed by these authors, the oil remaining was taken up in ether and precipitated by petroleum ether. The precipitate, on standing in the refrigerator, crystallized and was recrystallized from petroleum ether with alcohol added. The derivatives of glutamic and aspartic acids crystallized as silky needles (yield nearly quantitative), lysine also as silky needles (yield 20%), and proline as clear prisms (yield 50%). The arginine derivative was soluble in alcohol but insoluble in ether or petroleum ether. It has not been possible to cause this derivative to crystallize. The characteristics of these compounds are shown in Table II.

TABLE II

Amino acid	M. p. of deriv., °C.	Analyses, % Calcd.	Found	Calcd.	Found
d-Glutamic acid[21]	61–62	N 3.39	3.19	S 7.76	7.89
l-Aspartic acid[22]	64–65	N 3.51	3.35	S 8.03	8.17
d,l-Lysine[23,24]	111–113	C 56.42	56.28[25]	H 6.71	6.50[25]
l-Proline[26]	53–55	C 59.03	58.85[25]	H 7.13	6.90[25]
d-Arginine	Oil				

Acknowledgment.—One of us (E. W. M.) acknowledges with pleasure his indebtedness to: (1) Dr. H. B. Lewis, for the privilege of working in his laboratories at the University of Michigan, and for the gift of samples of several of the amino acids; (2) The Rockefeller Fund, an appropriation from which partly supported this investigation; (3) Dr. Wm. de B. MacNider, for the gift of a part of his research funds; (4) Dr. O. P. Wintersteiner, through whose courtesy certain of the analyses reported in Table II were made.

Summary

The *p*-toluenesulfonyl derivatives of nineteen amino acids have been prepared of which six have not been described previously. The *p*-toluenesulfonyl derivatives of aspartic acid, *d*-glutamic acid, *d,l*-lysine and *l*-proline did not crystallize. The non-crystalline derivatives, except tryptophane, were converted to their butyl esters and these crystallized, with the exception of arginine. The butyl esters of the derivatives of the four remaining amino acids are described for the first time in this paper.

CHAPEL HILL, N. C. RECEIVED JANUARY 28, 1937

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[20] *Cf.* also Gurin, THIS JOURNAL, **58**, 2104 (1936).

[21] That is, di-*n*-butyl [N-*p*-toluenesulfonyl]-*d*-glutamate.

[22] That is, di-*n*-butyl [N-*p*-toluenesulfonyl]-*l*-aspartate.

[23] That is, *n*-butyl [α,ε-di-*p*-toluenesulfonylamino]-*n*-caproate.

[24] Product contained a trace of ash; analytical data corrected for this.

[25] Analysis made under the direction of Dr. O. P. Wintersteiner.

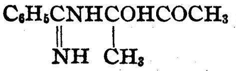
[26] That is, *n*-butyl [N-*p*-toluenesulfonyl]-*l*-pyrrolidine-α-carboxylate.

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

The Structure of Benzamidine-glyoxal and of its Compounds with Aromatic Aldehydes

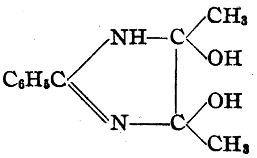
BY JOHN B. EKELEY AND ANTHONY R. RONZIO

In former papers[1] it has been shown that in alkaline solution aromatic amidines form addition products with glyoxal which can be isolated as the free bases or as their hydrochloride salts. In water solution the addition products are dissociated into amidine and glyoxal since from the solutions the osazone and dioxime of glyoxal can be obtained. We now have absorption spectra evidence which confirms this conclusion. We have exactly the same kind of evidence that the addition product from benzamidine and diacetyl obtained by Diels and Schleich[2] is, like that of benzamidine-glyoxal, an open chain compound as they assumed.



$C_6H_5C(=NH)NHC(OH)(CH_3)COCH_3$

and not



Inspection of the absorption spectra curves for benzamidine hydrochloride, benzamidine-glyoxal and benzamidine-diacetyl confirms the above statements.

There has been described[1] a long series of compounds which were obtained by the action of aromatic aldehydes upon aromatic amidines and glyoxal in alkaline solution. From the evidence then at hand we assumed them to contain either a pyrimidine or a glyoxaline ring. Ruhemann and Cunnington[3] prepared derivatives from benzamidine and phenylpropiolic ester, one of which, diphenylglyoxalidone, a yellow compound, pos-

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[1] Ekeley and Ronzio, THIS JOURNAL, **57**, 1353 (1935); Ekeley and Elliott, *ibid.*, **58**, 163 (1936).

[2] Diels and Schleich, *Ber.*, **49**, 1713 (1916).

[3] Ruhemann and Cunnington, *J. Chem. Soc.*, **75**, 954 (1899).

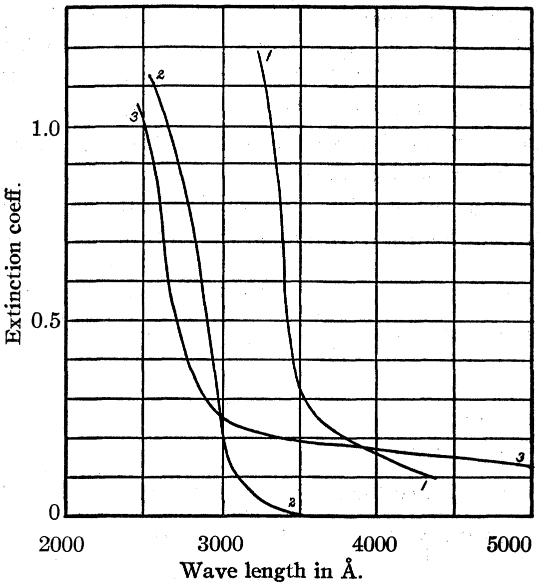

Fig. 1.—Curve 1, benzamidine·HCl·$2H_2O$, 0.0328 g./100 ml. of H_2O, 1-cm. cell; curve 2, benzamidine–glyoxal addition product, 0.00375 g./50 ml. of dioxane, 1-cm. cell; curve 3, benzamidine–diacetyl addition product, hydrochloride 0.00205 g./50 ml. of H_2O, 1-cm. cell.

sesses properties similar to the one obtained by us from benzaldehyde, benzamidine and glyoxal.

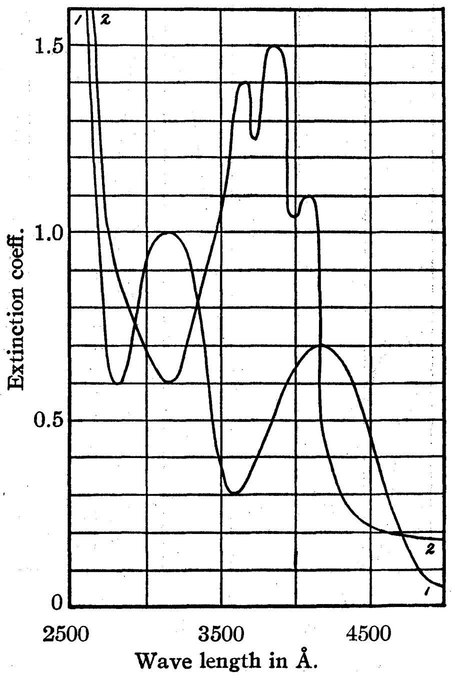

Fig. 2.—Curve 1, Ruhemann and Cunnington's glyoxalidone, 0.00090/50 ml. of KOH–95% E + OH soln., 1-cm. cell; curve 2, same, 0.00100 g./50 cc. of dioxane, 1-cm. cell.

The second compound they proved to be identical with Pinner's[4] diphenylhydroxypyrimidine. We have prepared these compounds and compared the absorption spectra curves obtained from them both in dioxane[5] and in dilute potassium hydroxide solution with the curves obtained from our benzaldehyde, benzamidine, glyoxal compound in the same solvents. The similarities between the curves from R. and C.'s glyoxalidone and those from our benzaldehyde-benzamidine–glyoxal compound are so very pronounced that we are forced to the conclusion that their structures are similar and that both have a glyoxaline ring in acid, basic, or neutral solution, the change from acid to alkaline solution bringing about a corresponding change in the two compounds, namely, to that of a tautomeric form.

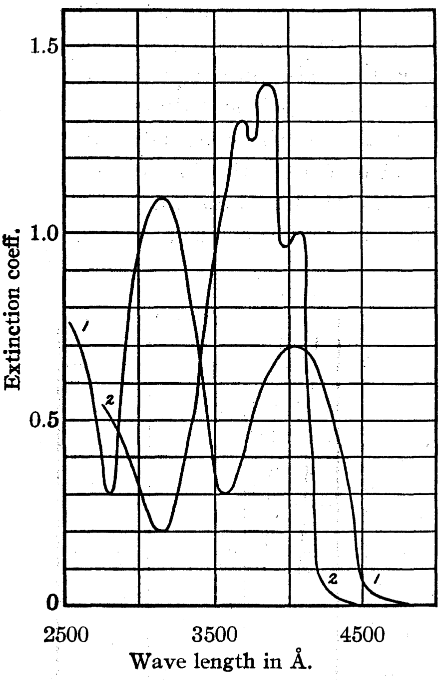

Fig. 3.—Curve 1, benzamidine–benzaldehyde–glyoxal compound, 0.00215 g./100 ml. of KOH–H_2O solutions, 1-cm. cell; curve 2, same, 0.00135 g./100 ml. of dioxane, 1-cm. cell.

The reactions involved in the formation of the condensation product between aromatic aldehydes, aromatic amidines and glyoxal are

$$\text{RCHO} + \text{OCHCHO} \longrightarrow \text{RCOCHOHCHO} \qquad (1)$$

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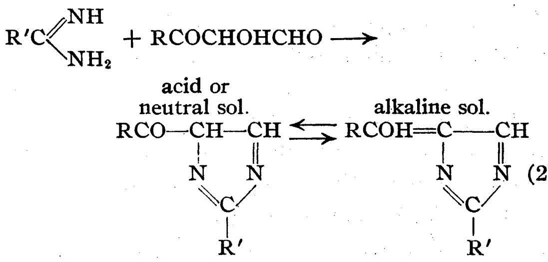
(4) Pinner, *Ber.*, **22**, 1612 (1889).

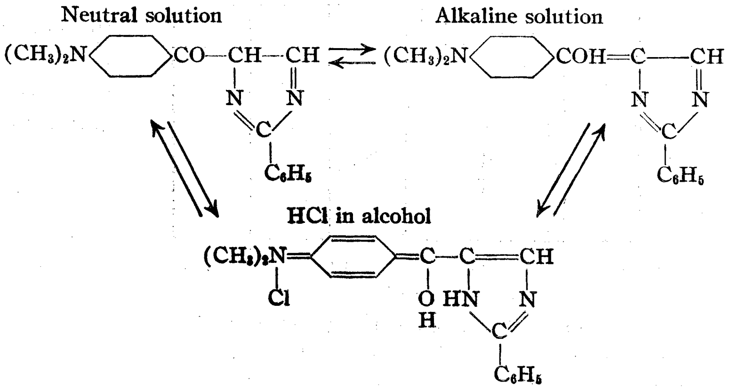
(5) Technical dioxane purified by the method of Oxford [*Biochem. J.*, **28**, 1325 (1934)] gives very faint narrow absorption bands at 2610, 2550, 2500 Å. These bands are too weak and narrow to interfere in absorption spectra work.



(2)

In one case out of forty-five compounds obtained from aromatic aldehydes, namely, that from *p*-dimethylaminobenzaldehyde, does the solution change color when made acid, especially in alcohol solution. In this case the color becomes deep red. The absorption spectrum curves show that the presence of the *p*-dimethylamino group in the original aromatic nucleus causes the loss of the characteristic triplet in dioxane solution, while in acid the curve suffers a further change and is shifted toward the red end of the spectrum. The changes in acid solution may be explained by the assumption of the formation of a quinonoid structure, while in alkaline solution the color is due to the presence of the fulvenoid chromophore alone.

From the mother liquor of the benzamidine-glyoxal addition product we obtained a small amount of an acid[1] which from the empirical formula we assumed to be a condensation product of glyoxylic acid, benzamidine and glyoxal, since



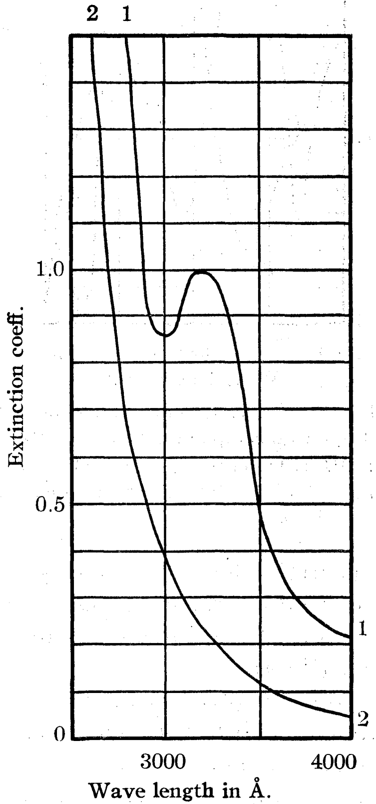


Fig. 4.—Curve 1, diphenylhydroxypyrimidine, 0.00170 g./50 ml. of dioxane, 1-cm. cell; curve 2, same, 0.00085 g./50 ml. of KOH–H₂O solution, 1-cm. cell.

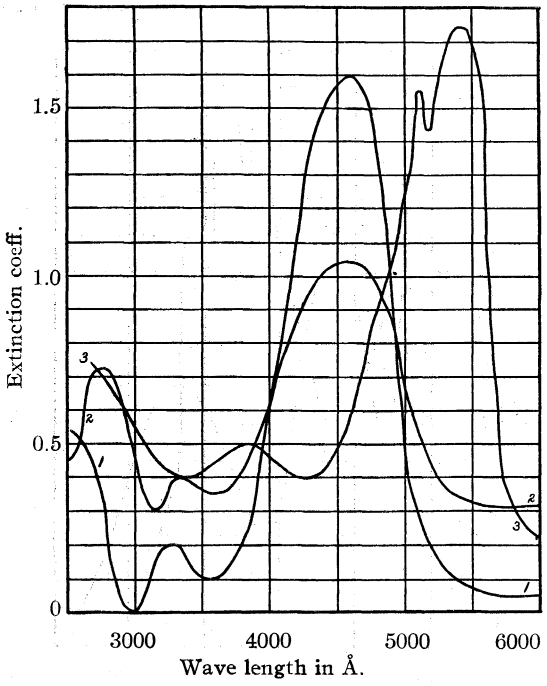
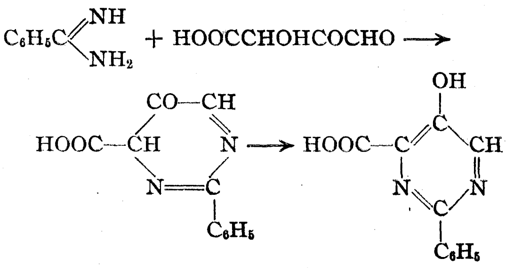


Fig. 5.—Curve 1, benzamidine–glyoxal–*p*-dimethylaminobenzaldehyde compound, 0.00056 g./50 ml. of dioxane, 1-cm. cell; curve 2, same, 0.00060 g./50 ml. of KOH–H₂O solution, 1-cm. cell; curve 3, same, 0.00067 g./50 ml. of 95% ethyl alcohol containing 1 cc. of concd. HCl, 1-cm. cell.

the glyoxal used contained glyoxylic acid together with oxalic acid. The same compound in a 75% yield was then prepared from glyoxylic acid (prepared by the method of Tafel and Friedrichs[6]) and benzamidine-glyoxal. They were both recrystallized from alcohol–water solution, m. p. 255°. *Analyses.* Calcd. for $C_{11}H_8N_2O_3$, compound from mother liquor: C, 61.11; H, 3.70; N, 12.95. Found: C, 61.50; H, 3.90; N, 12.82. Compound from glyoxylic acid and benzamidineglyoxal, found: C, 61.00; H, 3.90; N, 13.08.

Comparison of the absorption spectrum curve of this compound with that of Pinner's diphenylhydroxypyrimidine reveals such striking similarities that we must assign to this acid the pyrimidine structure, so that in this case the compound is phenylhydroxypyrimidine carboxylic acid. The formation of the acid would seem to be according to the following reactions

$$\mathrm{HOOCCHO + OHCCHO = HOOCCHOHCOCHO} \quad (1)$$



(2)

The absorption spectra curves herein given were obtained using a Hilger E3 quartz spectrograph, a Hilger sectorphotometer and a high frequency under-water spark. Eastman panchromatic plates were used. In plotting the curves we used wave lengths as abscissas and "extinction coefficients" as ordinates.

Summary

1. Absorption spectra data are in accord with chemical data pointing to an open chain formula for the addition products of aromatic amidine and glyoxal and for those of benzamidine with diacetyl.

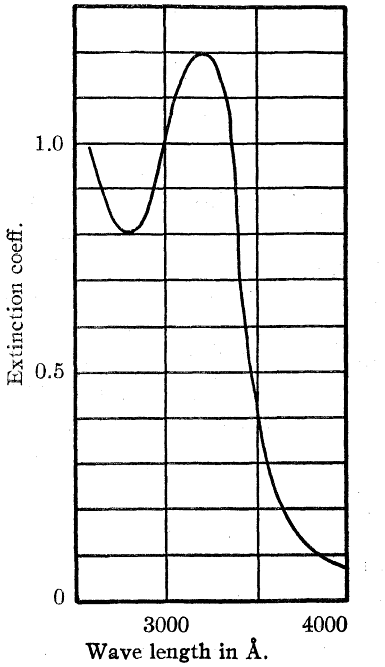


Fig. 6.—Glyoxylic acid–benzamidine-glyoxal compound, 0.00170 g./50 ml. of dioxane, 1-cm. cell.

2. The structures of the compounds formed from aromatic aldehydes, aromatic amidines and glyoxal are generally phenylbenzoylglyoxalines in acid or neutral solution and existing in a tautomeric form in alkali solutions.

3. The compound derived from *p*-dimethylaminobenzaldehyde, benzamidine and glyoxal gives absorption spectra curves in dioxane in which the characteristic triplet has become a single band, in alkaline solution it suffers a further change and in hydrochloric acid solution is shifted toward the red probably due to the formation of a quinonoid ring.

4. The compound derived from glyoxylic acid gives absorption spectra similar to diphenylhydroxypyrimidine, hence is assumed to be a phenylhydroxypyrimidine carboxylic acid.

BOULDER, COLORADO RECEIVED MARCH 18, 1937

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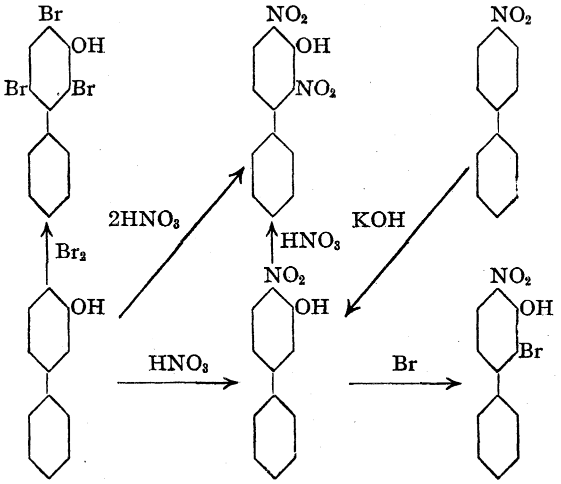
[6] Tafel and Friedrichs, *Ber.*, **37**, 3187 (1904).

[Joint Contribution from the Chemistry Department of the University of Oklahoma and the Laboratories of the Monsanto Chemical Company]

Derivatives of the Hydroxydiphenyls. III. 4-Nitro-3-hydroxydiphenyl

By J. C. Colbert, Wyman Meigs and R. L. Jenkins

In the 4-hydroxydiphenyl molecule the usual orienting effect of the hydroxyl group should open positions 3,5,4′ to substitution. That substitution does follow the normal course, namely, (1) mono-ortho, (2) di-ortho, and (3) di-ortho-*p*′ has been demonstrated by Bell and Robinson[1] for nitration, and by Colbert and others[2] for chlorination. The substitution reactions of 2-hydroxydiphenyl, in which postions 3,5 are open, have been investigated by Borsche and Scholten.[3]



Very little work has been reported for the less readily obtainable 3-hydroxydiphenyl. This latter phenol presents an interesting case since positions 2,4,6 are open on the same ring with the hydroxyl group—a circumstance which should lead to the preparation of phenyl substituted picric acid as well as like compounds.

Nitration and Bromination of 3-Hydroxydiphenyl.—When 3-hydroxydiphenyl is treated in acetic acid solution with one molar proportion of nitric acid, the solution warms up, turns a deep red, and when added to boiling water throws down a crystalline precipitate of mononitro-3-hydroxydiphenyl. Further dilution of the mother liquor leads to precipitation of a dark colored oil, the nature of which is still under investigation. Nitration with two or more molar proportions of nitric acid yields a dinitro derivative. This is the highest nitration product it has yet been possible to obtain by the direct nitration of 3-hydroxydiphenyl. Since this dinitro derivative does not form a diphenyl ether, or a benzoate, reactions given readily by the mononitro-3-hydroxydiphenyl, it is thought to be a di-ortho derivative and is tentatively assigned the structure 2,4-dinitro-3-hydroxydiphenyl. It should be pointed out that this lack of reactivity is also found in the case of 3,5-dinitro-4-hydroxydiphenyl as we have often observed in this Laboratory. The nitration of mononitro-3-hydroxydiphenyl forms the same dinitro derivative as that obtained by use of a double portion of nitric acid upon 3-hydroxydiphenyl.

Bromination in carbon disulfide of 3-hydroxydiphenyl yields oils save when three or more molar proportions of bromine are added. In the latter case a crystalline tribromo derivative results. The formula 2,4,6-tribromo-3-hydroxydiphenyl is assigned tentatively although it has not yet been possible to degrade to recognizable products. While mononitro-3-hydroxydiphenyl brominates readily in acetic acid solution, only one bromine atom enters the ring. Henkel and Hey[4] report the preparation of 5-bromo-3-hydroxydiphenyl and 4,5-dibromo-3-hydroxydiphenyl, but not by direct bromination of the corresponding phenol.

Proof of Structure for 4-Nitro-3-hydroxydiphenyl.—Wohl[5] has shown that when nitrobenzene is allowed to stand in contact with finely powdered potassium hydroxide an intermolecular oxidation–reduction reaction occurs which gives rise to *o*-nitrophenol as one of the principal products of the reaction. It has also been shown[6] that on the large scale and with special care to avoid the presence of moisture the principal reaction comprises the interaction of five moles of nitrobenzene in the presence of the potassium hydroxide to form three moles of nitrophenol, in the form of the potassium salt, and one mole of azoxybenzene. A relatively small amount of the *p*-nitrophenol is produced at the same time.

The reaction appears to be fairly general, hav-

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[1] Bell and Robinson, *J. Chem. Soc.*, **130**, 1128 (1927).

[2] Colbert and others, This Journal, **56**, 202 (1934).

[3] Borsche and Scholten, *Ber.*, **50**, 596 (1917).

[4] Henkel and Hey, *J. Chem. Soc.*, **131**, 1200 (1928).

[5] Wohl, *Ber.*, **32**, 3486 (1899).

[6] Wohl and Aue, *ibid.*, **34**, 2444, footnote (1901).

ing been used to convert nitrotoluene, *m*-nitrochlorobenzene and nitronaphthalene to the corresponding *o*-nitrophenols[7] but it has not, so far as we are aware, been applied to a nitrodiphenyl.

When 4-nitrodiphenyl is heated on the water-bath with an excess of powdered potassium hydroxide, the medium being benzene, a nitrophenol is obtained. The melting point as well as the microscopic appearance of this phenol is in agreement with the mononitrophenol obtained by the direct nitration of 3-hydroxydiphenyl. A mixed melting point confirms this conclusion. Since introduction of the hydroxyl group into 4-nitrodiphenyl yields the same phenol as that obtained by introducing the nitro group into 3-hydroxydiphenyl, the nitrophenol must be 4-nitro-3-hydroxydiphenyl.

The nature of the oil formed in the mononitration of 3-hydroxydiphenyl is still under investigation. The oil may contain the 2-nitro, the 5-nitro or a mixture of such mononitro derivatives. Preliminary experiments indicate that when 2-nitrodiphenyl is treated with potassium hydroxide, a mononitrophenol is formed. This compound may be found identical with a component of the oil.

Experimental Part

4-Nitro-3-hydroxydiphenyl from 3-Hydroxydiphenyl.—Seven grams of 3-hydroxydiphenyl was dissolved in 100 cc. of glacial acetic acid, the solution cooled to 10–15° and 2.6 cc. of concd. nitric acid in 20 cc. of glacial acetic acid added. The solution became a dark red within two minutes and after standing for thirty minutes at room temperature was precipitated by pouring with stirring into an equal volume of boiling water. The solution was allowed to cool and the rather small precipitate of irregular yellow plates filtered. The yield varied from 15.6 to 24.4%, the larger figure being obtained by permitting the nitration mixture to stand overnight before precipitation. The larger yields were darker colored and somewhat tarry. Recrystallization from 80% alcohol gave a product melting from 102.5–103.5°.

Anal. Calcd. for $C_{12}H_9NO_3$: N, 6.52. Found: N, 6.80.

4-Nitro-3-hydroxydiphenyl from 4-Nitrodiphenyl.—Two hundred and eighty-four grams of potassium hydroxide, previously ground in a corn mill, 112 g. of benzene and 112 g. of 4-nitrodiphenyl were well mixed and heated on the water-bath at 72–76° for seventy-two hours. At the end of that time a small amount of water and benzene was added with good agitation and the mixture filtered. It was finally pulped twice with fresh benzene and the benzene filtered off after each pulping. Weight of air-dried precipitate was 45 g.

The precipitate was dissolved in 500 cc. of hot water, the solution filtered hot and allowed to cool slowly. The deep red, crystalline, precipitate was filtered off, washed with a little cold water, and dried in a desiccator; weight 18.1 g.

A small portion (4 g.) of this material was dissolved in water and the solution acidified with hydrochloric acid, whereupon a greenish-yellow crystalline solid precipitated. After being filtered off, washed and dried, the material weighed 3.0 g. and melted at 103.1 to 103.2°. It was recrystallized from 20 g. of Skellysolve E. The recrystallized material occurred in the form of glistening greenish-yellow plates, weighed 2.5 g. and melted at 103.1 to 103.3°.

When a sample of this material was mixed with that obtained by direct nitration of 3-hydroxydiphenyl, the m. p. was 102.7 to 103.2°. When crystallized from 80% alcohol and examined under the microscope the crystals from the two sources appeared identical.

Dinitro-3-hydroxydiphenyl.—Seven grams of 3-hydroxydiphenyl was dissolved in 20 cc. of glacial acetic acid and 7.8 cc. of concd. nitric acid added. This was sufficient nitric acid for the formation of a trinitro derivative. The solution became red and boiled vigorously. Upon cooling coarse yellow, prismatic crystals precipitated and 2.95 g. of product was obtained, or a yield of 27.5%. Evaporation of the mother liquor to half volume led to the further crystallization of less pure material. Recrystallization from 95% alcohol gave a lemon-yellow product melting at 172.5–173°. This compound is very inert chemically and forms neither benzoate, bromo derivative, nor diphenyl ether.

Dinitro-3-hydroxydiphenyl from 4-Nitro-3-hydroxydiphenyl.—Six-tenths gram of 4-nitro-3-hydroxydiphenyl was dissolved in 8 cc. of glacial acetic acid and 0.25 cc. of concd. nitric acid in 3.0 cc. of glacial acetic acid added. After standing a few minutes the solution was heated to boiling, cooled to 15° and precipitated by pouring over ice. The precipitate weighed 0.54 g., m. p. 165°. Recrystallization from 95% alcohol raised the m. p. to 170°. A mixed melting point confirmed the identity of the product from the two sources.

Anal. Calcd. for $C_{12}H_8N_2O_5$: N, 10.76. Found: N,10.30.

Tribromo-3-hydroxydiphenyl.—When 28.2 g. (8.9 cc.) of bromine was added to 10.0 g. of 3-hydroxydiphenyl in 100 cc. of carbon disulfide, the ensuing reaction was quite vigorous. After standing for five days the solution was washed with sodium carbonate solution, acidified, separated, and dried over calcium chloride. The carbon disulfide was distilled off and crystals obtained after long standing. The product was light brown, slightly gummy, and formed in 86.1% yield, *i. e.*, 20.62 g. Recrystallization was accomplished with difficulty from 200 cc. of 80% acetic acid; m. p. 92°.

Anal. Calcd. for $C_{12}H_7OBr_3$: Br, 58.93. Found: Br, 58.10.

Other Derivatives of 3-Hydroxydiphenyl.—Ethers and other derivatives have been obtained by methods similar to those reported in a preceding paper.

3′-Phenyl-2,4-dinitrodiphenyl ether, $C_6H_5C_6H_4OC_6H_3(NO_2)_2$, from potassium hydroxide, pyridine, $C_6H_3Cl(NO_2)_2$; m. p. 100°; yield 90.0%; calcd. N, 8.33; found: N, 8.53.

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[7] German Patent 116,790 (1899).

3′-Phenyl-2,4,6′-trinitrodiphenyl ether, $C_6H_5C_6H_3(NO_2)OC_6H_3(NO_2)_2$, from potassium hydroxide, pyridine, $C_6H_3Cl(NO_2)_2$; m. p. 131°; yield 95.7%; calcd. N, 11.03; found: N, 10.99.

3′-Phenyl-2,4,6-trinitrodiphenyl ether, $C_6H_5C_6H_4OC_6H_2(NO_2)_3$, from potassium hydroxide and picryl chloride; m. p. 143°; yield 92.4%; calcd. N, 11.03; found: N, 11.80.

?-Bromo-4-nitro-3-hydroxydiphenyl, $C_6H_5C_6H_2Br(NO_2)OH$; m. p. 109°; yield 40.0%; calcd. Br, 27.18; found: Br, 26.62.

Summary

1. When 3-hydroxydiphenyl is nitrated the first compounds formed are probably isomeric mononitro derivatives. One of these isomers has been isolated in pure form.

2. The structure of the mononitro derivative isolated has been proved by preparation from 4-nitrodiphenyl by the use of powdered potassium hydroxide.

3. While with bromine 3-hydroxydiphenyl yields a tribromo derivative, with nitric acid only a mono and a dinitro compound have been prepared. Due to the reduced activity of the hydroxy group the dinitrophenol is believed to be 2,4-dinitro-3-hydroxydiphenyl.

4. Work is continuing in an effort to obtain higher nitro derivatives, bromo derivatives containing less than three bromine atoms, and in the expectation of obtaining definite compounds from the oily by-product obtained in the mononitration of 3-hydroxydiphenyl.

NORMAN, OKLAHOMA RECEIVED APRIL 22, 1937

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Crystalline Acetal Derivatives of *d*-Arabinose[1]

BY EDNA M. MONTGOMERY, RAYMOND M. HANN AND C. S. HUDSON

Solutions of methyl glycoside acetates of the pyranose type, such as β-methyl glucoside tetraacetate, in a mixture of acetic acid and acetic anhydride, upon catalysis by sulfuric acid, have been shown to be transformed to α-acetates of the pyranose type,[2] while those possessing a furanoside linkage are changed under the same conditions to form either aldehydo acetates[3] or ring acetates probably of furanoid structure. It seemed of interest to investigate the course of this reaction in the case of an acetylated methyl glycoside of arabinose, in which the ring, while pyranoid in structure, involves the hydroxyl group of the terminal carbon atom. The results obtained were so novel that it seemed desirable to extend the investigation to include observations upon the catalytic effect of zinc chloride; here again, a novel change was disclosed.

A solution of triacetyl-β-methyl-*d*-arabinoside (I) in a mixture of three volumes of acetic acid and seven volumes of acetic anhydride (hereafter called the acetylating mixture), containing 4% by weight of sulfuric acid, reached an equilibrium rotation (−17°)[4] in three minutes at 20°, in contrast to the behavior of tetraacetyl-β-methyl glucoside, which required forty-eight hours under the same conditions. The crystalline reaction products that were isolated from the pentose derivative included 56% of an open chain compound, aldehydo-*d*-arabinose hexaacetate (II), but there was present only 11% of the expected ring compound, β-*d*-arabinose tetraacetate (III); under similar conditions β-methyl glucoside tetraacetate yielded 92% of the ring compound, α-glucose pentaacetate.

The fact that this concentration of sulfuric acid thus led largely to rupture of the pentopyranoside ring, removal of the methyl group, and peracetylation, suggested the substitution of zinc chloride or a weaker sulfuric acid concentration as milder catalytic agents. The zinc chloride (8%) caused a decided shift in the equilibrium value (+30°) of the acetylating solution and resulted in *complete* rupture of the lactonyl ring, ***but without removal of the methyl group***, the elements of acetic anhydride being added to yield a mixture of two pentaacetyl-*d*-arabinose methyl hemi-acetals (IV and V), which were isolated in high (86%) yield. No ring compound could be isolated and the rotations of the pure hemi-acetal pentaacetates, +25° and +32° (in the acetylation mixture), compared to the equilibrium rotation of +30°, indicated the

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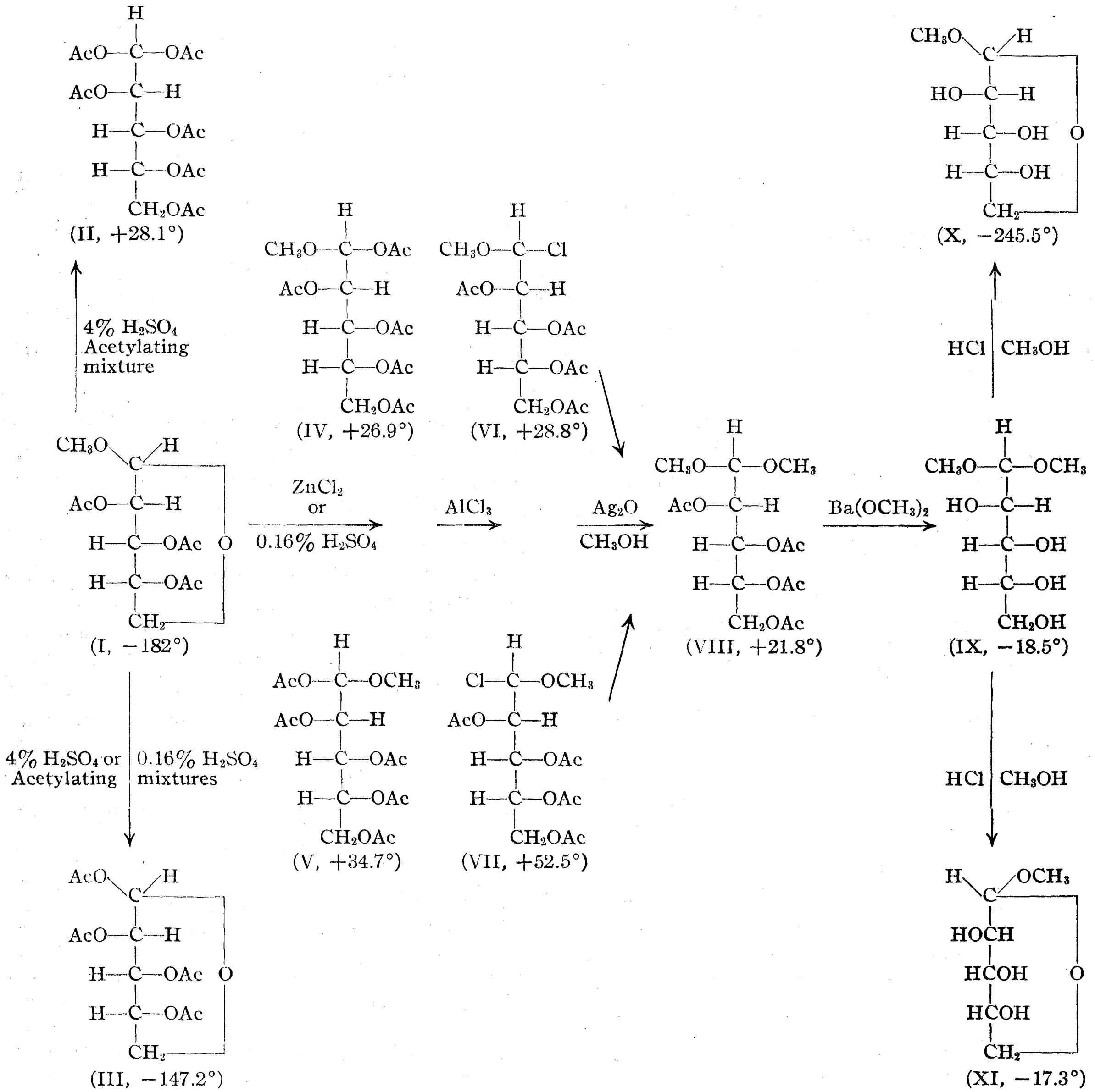
[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] Hann and Hudson, THIS JOURNAL, 56, 2465 (1934).

[3] Montgomery and Hudson, *ibid.*, 56, 2463 (1934).

[4] All rotations are specific rotations at 20° in sodium light.



absence of a levorotating reaction product. The diastereomers, moreover, are interconvertible in the zinc chloride solution, reaching an equilibrium value of +28° and being present in approximately equal amounts. They are quantitatively converted to aldehydo-*d*-arabinose hexaacetate by the 4% sulfuric acid solution, indicating their formation as an intermediate step in the production of the latter substance from β methyl-*d*-arabinoside triacetate when dissolved in this solution.

The weaker sulfuric acid (0.16%) brought about the same equilibrium value (−17°) obtained with the stronger acid, and examination of the reaction products indicated a comparable degree of ring rupture since it was possible to isolate β-*d*-arabinose tetraacetate in a yield of only 8% of the theoretical; however, with this weaker acid concentration removal of the methyl groups *did not* occur from the simultaneously formed isomeric pentaacetyl-*d*-arabinose methyl hemi-acetals and they were isolated as the main reaction products. The agreement of the equilibrium rotations for the weaker and the stronger acid catalysts is thus fortuitous and is due to the fact that the rotations of the aldehydo hexaacetate and the two pentaacetyl methyl hemi-acetals are nearly alike.

The results obtained with the various catalysts are summarized in Table I, which also includes ob-

TABLE I

RESULTS OF CATALYTIC TRANSFORMATION OF ACETYLATED *d*-ARABINOSE DERIVATIVES

Substance	Rotation in non-catalyzed acetylating mixture	Rotation in acetylating mixture + 8% $ZnCl_2$	Products	Rotation in mixture + 0.16% H_2SO_4	Products	Rotation in mixture + 4% H_2SO_4	Products
β-Methyl-*d*-arabinoside triacetate	−184°	+30° (48 hrs.)	42% IV 44% V	−17° (4 hrs.)	21% IV 20% V 8% III	−17° (3 min.)	56% II 11% III
α-Methyl-*d*-arabinoside triacetate	− 19°	+30° (12 hrs.)	37% IV 37% V	−25° (5 hrs.)	18% IV 18% V 8% III	−25° (20 min.)	50% II 14% III
Pentaacetyl-*d*-arabinose methyl hemi-acetal IV	+ 25°	+28°	46% IV 44% V	+27°	44% IV 42% V	+25°	91% II
Pentaacetyl-*d*-arabinose methyl hemi-acetal V	+ 32°	+28°	48% IV 46% V	+27°	40% IV 42% V	+25°	92% II

servations upon α-methyl-*d*-arabinoside triacetate and the changes of the hemi-acetal pentaacetates in catalyzed acetylating mixtures. These data indicate that zinc chloride catalysis slowly but completely ruptures the ring and introduces an acetyl radical at each of carbon atoms 1 and 5 without breaking the methoxyl union; 0.16% sulfuric acid produces much more rapidly an equilibrium between a small amount of a ring acetate and the interconvertible open chain methyl hemi-acetal pentaacetates; and 4% sulfuric acid is believed to bring about very rapidly the same equilibrium as the dilute acid and then to remove, also rapidly, the methyl group of the hemi-acetals which is followed by acetylation to yield the aldehydrol hexaacetate.

Whether these reactions which rupture the oxygen ring are a specific property of the arabinose configuration or are a general reaction of pyranoside linkages involving a terminal carbon atom is at present left undecided; further studies on this subject will be made.

It would be anticipated that the acetyl group in combination with the aldehydic carbon in a pentaacetyl-*d*-arabinose methyl hemi-acetal could be differentially substituted by halogen. Treatment of the two pure isomeric acetylated hemi-acetals with anhydrous aluminum chloride formed two different crystalline isomeric tetraacetyl-*d*-arabinose-1-chloro-1-methyl acetals (VI and VII). Upon solution in methyl alcohol and treatment with silver oxide these two compounds yielded the same crystalline tetraacetyl-*d*-arabinose dimethyl acetal (VIII) which could be deacetylated readily to form *d*-arabinose dimethyl acetal in quantitative yield. Hydrolysis of the dimethyl acetal in 0.05 *N* aqueous acid led to the isolation of crystalline *d*-arabinose, while the action of acid methyl alcohol gave a mixture of methyl-*d*-arabinosides (X and XI), the latter reaction being consonant with Fischer's view that dimethyl acetals may be one of the intermediate products in the synthesis of glycosides.

We are indebted to Dr. O. E. May of the Industrial Farm Products Laboratory, U. S. Department of Agriculture, for a supply of calcium gluconate, to Mr. George L. Keenan, of the Food and Drug Administration, U. S. Department of Agriculture, for optical-crystallographic examination of crystals, and to Dr. W. T. Haskins, of the National Institute of Health, for microchemical analyses of some of the described compounds.

Experimental

General.—The 4% acid acetylation solution was prepared by adding 4% by weight of concentrated sulfuric acid dropwise to an ice cold mixture of 70 cc. of acetic anhydride (99.5%) and 30 cc. of acetic acid (99.5%). The weak acid solution (0.16%) was prepared by diluting the 4% acid solution with the anhydride–acid mixture. The zinc chloride solution contained 8 g. of the fused salt in 100 cc. of the anhydride acid mixture. All polarimetric observations of the acetylating reaction were made at 20 ± 0.5° in a 1-dm. glass polariscope tube with sealed glass end-plates. Specific rotations of pure compounds were measured in 2-dm. tubes in the specified solvent.

Transformation of Triacetyl-β-methyl-*d*-arabinoside in the 4% Acid Acetylating Mixture. Isolation of Aldehydo-*d*-arabinose Hexaacetate.—A solution of 10 g. of triacetyl-β-methyl-*d*-arabinoside in 250 cc. of the strong acid reagent changed in rotation from −184° to a constant equilibrium value of −17° in three minutes at 20°. After standing twenty-four hours, the solution was poured into crushed ice, yielding 7.0 g. of a crystalline precipitate (rotation, +26° in chloroform). Extraction of the aqueous solution yielded 5.8 g. of sirup (rotation, −60° in chloroform) which slowly deposited about 3 g. of crystalline material. The combined crystals were fractionally recrystallized from a mixture of 20 cc. of alcohol and 10 cc. of water, yielding 8.2 g. (56%) of aldehydo-*d*-arabinose hexaacetate and 1.2 g. (11%) of β-*d*-arabinose tetraacetate.

Aldehydo-*d*-arabinose hexaacetate crystallizes from 3 parts of 70% alcohol in needles melting at 89.5° (corr.). Its specific rotation in chloroform is +28.1° (*c*, 1.33), comparable in value with but opposite in sign to Wolfrom's[5] observation of −27° for the 1-isomer which also melts at 89.5°.

Optical-crystallographic examination by Mr. G. L. Keenan showed the crystals to be rodlike, many with six sides. The refractive indices were $n_\alpha = 1.455$, $n_\beta = 1.472$ and $n_\gamma = 1.495$, all ±0.003. In parallel light with crossed nicols the extinction was straight, the double refraction strong, the sign of elongation ±, and in convergent parallel light interference figures were rare.

Anal. Calcd. for $C_5H_6O_6(COCH_3)_6$: C, 48.6; H, 5.8; acetyl, 14.28 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 48.8; H, 6.0; acetyl, 14.25 cc.

Transformation of Triacetyl-β-methyl-*d*-arabinoside in the 8% Zinc Chloride Acetylating Mixture. Isolation of Two Isomeric Crystalline Pentaacetyl-*d*-arabinose Methyl Hemi-acetals.—A solution of 10 g. of the acetylated methyl glycoside in 125 cc. of the zinc chloride reagent slowly changed in specific rotation from −184° to an equilibrium value of +30° in forty-eight hours at 20°. The slightly yellow solution was poured into one liter of ice water and after decomposition of the excess acetic anhydride the solution was extracted with chloroform. The solvent-free sirup that was obtained (13 g.) by removal of the chloroform was dissolved in 30 cc. of absolute ether and after one week crystallization of clusters of rodlike prisms, rotating +26.9° in chloroform when pure, occurred in a yield of 5.7 g. (42%). From the mother liquors a crop of a second type of prisms, short, many faced with one pyramidal end, rotating +34.7° in chloroform when pure, was recovered in an amount of 5.9 g. (44%). Upon analysis these substances proved to be isomeric, and contained one methoxyl and five acetyl groups. These facts and other evidence to be presented indicated their structure as pentaacetyl-*d*-arabinose methyl hemi-acetals. Their isomerism is due to the stereo-arrangement of the groups attached to carbon atom I. In further discussion the compound rotating +26.9° will be designated the first isomer, and the one of rotation +34.7° the second isomer. It is emphasized however that the assignment of the relative stereo positions of the methoxyl and acetyl groups on the aldehyde carbon atom in the hemi-acetal formulas is arbitrary.

The first isomer, when recrystallized to constant physical properties from ether, melted at 76° and showed a specific rotation of +26.9° in chloroform (*c*, 1.33). It was very soluble in the usual organic solvents, insoluble in petroleum ether, and soluble in water to the extent of 0.6 g. in 100 cc. at 20°. It reduced Fehling's solution slowly on boiling. Optical-crystallographic examination by Mr. Keenan showed that in ordinary light the refractive indices of the crystals were: $n_\alpha = 1.448$, $n_\beta = 1.500$, $n_\gamma = 1.510$, all ±0.003. In parallel light, with crossed nicols, the double refraction was very strong. In convergent polarized light, crossed nicols, biaxial interferences figures showing sections normal to the acute bisectrix were common, the axial angle being large, 2E = 70° (±5°). The optic sign was negative.

Anal. Calcd. for $C_5H_6O_5(OCH_3)(COCH_3)_5$: C, 49.0; H, 6.2; OCH_3, 7.9; acetyl, 12.75 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.1; H, 6.2; OCH_3, 7.9; acetyl, 12.70 cc.

The second isomer when pure melted at 68–70°, gave a specific rotation in chloroform of +34.7° (*c*, 1.33) and showed the same solubility behavior as the first isomer. Optical-crystallographic examination by Mr. Keenan showed that its optical properties are distinctly different, the refractive indices being $n_\alpha = 1.455$, $n_\beta = 1.464$, $n_\gamma = 1.490$, all ±0.003. In convergent polarized light, crossed nicols, partial biaxial interference figures are frequently obtained, usually showing sections normal to an optic axis or oriented obliquely to the bisectrices. The double refraction is strong.

Anal. Calcd. for $C_5H_6O_5(OCH_3)(COCH_3)_5$: C, 49.0; H, 6.2; OCH_3, 7.9; acetyl 12.75 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.0; H, 6.0; OCH_3, 7.9; acetyl, 12.65 cc.

Transformation of Triacetyl-β-methyl-*d*-arabinoside in 0.16% Acid Acetylating Mixture.—A solution of 10 g. of the acetylated glycoside in 250 cc. of the acetylating mixture declined in rotation from −184 to −17° in four hours at 20°. The solution was worked up in the usual manner and the resulting sirup brought to crystallization by solution in 30 cc. of ether and addition of 10 cc. of petroleum ether. The first yield was fractionally recrystallized, and 2.8 g. (21%) of the first and 2.7 g. (20%) of the second isomeric acetylated methyl hemi-acetals were obtained. The remaining sirup was taken up in 20 cc. of 50% alcohol and upon long standing at 5° separated 0.85 g. (8%) of β-*d*-arabinose tetraacetate.

Transformation of Triacetyl-α-methyl-*d*-arabinoside in Acetylating Mixtures.—Triacetyl-α-methyl-*d*-arabinoside was obtained as a colorless sirup rotating −17° in chloroform by the action of methyl alcohol and silver carbonate on crystalline acetobromo-*d*-arabinose. (1) A solution of 5 g. of the sirup in 67 cc. of the zinc chloride reagent changed slowly from an initial rotation of −19° to an equilibrium value of +30° in about twelve hours. No rise in rotation in a levo direction was observed, indicating the absence of an α to β shift prior to the breaking of the lactonyl ring (contrast the action of acid mixtures). The isolable reaction products were 2.5 g. (37%) of each of the isomeric acetylated methyl hemi-acetals. The rotational behavior and equilibrium value indicated the absence of a ring tetraacetate. (2) A solution of 10 g. of the sirup in 250 cc. of 0.16% acid reagent rose rapidly in rotation from −19 to −116° within forty minutes and then declined slowly to an equilibrium value of −25° at the end of five hours. The products isolated were 2.5 g. (18%) of each of the crystalline acetylated methyl hemi-acetals and 0.9 g. (8%) of β-*d*-arabinose tetraacetate. The ring acetate was isolated in only one case because of the extreme difficulty in getting it to crystallize, but the rotational data in all experiments of this group indicated its presence. (3) A solution of 5 g. of the sirup in 125 cc. of 4% acid reagent rose sharply in rotation from −19 to −114° in one minute and declined to an equilibrium value of −25° at the end of twenty minutes. The products isolated were 3.6 g. (50%) of aldehydo-*d*-arabinose hexaacetate and 0.8 g. (12%) of β-*d*-arabinose tetraacetate. A second experiment was interrupted at the rotation peak

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(5) Wolfrom, THIS JOURNAL, **57**, 2498 (1935).

of −114° and yielded 1 g. (14%) of crystalline β-methyl-*d*-arabinoside triacetate. The experiments on the α-acetylated glycoside confirm in every instance the similar experiments on the crystalline β-isomer.

Transformation of the Pentaacetyl-*d*-arabinose Methyl Hemi-acetals in Acetylating Mixtures.—(1) A solution of 5 g. of the first isomer (+26.9°) in 67 cc. of the zinc chloride reagent reached an equilibrium rotation of +28° within three minutes. From the reaction mixture 2.3 g. (46%) of unchanged material and 2.2 g. (44%) of the second isomer (+34.7°) was recovered. A similar experiment using 5 g. of the second isomer resulted in the same equilibrium rotation and yielded 2.4 g. (48%) of unchanged material and 2.3 g. (46%) of the first isomer. (2) A solution of 2.0 g. of the first isomer (+26.9°) in 50 cc. of the 0.16% acid mixture gave an equilibrium rotation of +26.8° after two minutes. The reaction products were 0.88 g. (44%) of the second isomer and 0.85 g. (42%) of the first isomer. The second isomer (+34.7°) in a similar experiment gave an equilibrium rotation of +27° in two minutes, the reaction products being 0.80 g. (40%) of the first isomer and 0.85 g. (42%) of the second one. No evidence was obtained of the presence of ring isomers. (3) A solution of 5.0 g. of the first isomer in 125 cc. of the 4% acid mixture showed no change in rotation from an initial value of +25° upon standing for eighteen hours. From the reaction mixture aldehydo-*d*-arabinose hexaacetate was recovered in a yield of 4.9 g. (91%). A similar experiment with the second isomer showed a change in rotation from +32 to +25° and yielded 5.0 g. (92%) of the aldehydo-*d*-arabinose hexaacetate.

2,3,4,5-Tetraacetyl-1-chloro-*d*-arabinose Methyl Hemi-acetal from Pentaacetyl-*d*-arabinose Methyl Hemi-acetal of Rotation +26.9° (the First Isomer).—A solution of 10 g. of the first isomeric acetylated hemi-acetal in 100 cc. of anhydrous alcohol-free chloroform was cooled to 5° and 10 g. of pulverized anhydrous aluminum chloride added, with gentle agitation; a light brown granular addition product separated. After one-half hour the mixture was washed with ice and water and the chloroform layer was dried with calcium chloride and concentrated *in vacuo* to a sirup, which separated crystalline material upon solution in 20 cc. of ether and addition of 10 cc. of petroleum ether. The crude product was recrystallized once in the same way, yielding 6.3 g. (67%). The compound melts at 71° (corr.) and shows a specific rotation of +28.8° in chloroform (*c*, 1.33). It is quite unstable, decomposing slightly upon recrystallization, and quite rapidly upon standing. A confirmatory experiment was conducted by Freudenberg's[6] method, yielding 65% of the chloro compound, melting at 70° and having a rotation of +29°.

Anal. Calcd. for $C_{14}H_{21}O_9Cl$: Cl, 9.6; OCH_3, 8.4. Found: Cl, 8.8; OCH_3, 7.8.

The Isomeric 2,3,4,5-Tetraacetyl-1-chloro-*d*-arabinose Methyl Hemi-acetal from Pentaacetyl-*d*-arabinose Methyl Hemi-acetal of Rotation +34.7° (the Second Isomer).—Under the same experimental conditions of chlorination by aluminum chloride the second isomeric acetylated hemi-acetal yielded 73% of a second chloro tetraacetyl methyl hemi-acetal melting at 73° (corr.) and showing a rotation of +52.5° in chloroform. The Freudenberg procedure gave a yield of 60% of the same product.

Anal. Calcd. for $C_{14}H_{21}O_9Cl$: Cl, 9.6; OCH_3, 8.4. Found: Cl, 8.8; OCH_3, 7.4.

Tetraacetyl-*d*-arabinose Dimethyl Acetal.—(1) A solution of 10 g. of crystalline tetraacetyl-1-chloro-*d*-arabinose methyl hemi-acetal, of rotation +28.8°, in a mixture of 25 cc. of absolute ether and 25 cc. of methyl alcohol was cooled to 0° and agitated with 10 g. of silver oxide. After five minutes, the separated silver salts were removed, the solution was concentrated to a sirup, the sirup was dissolved in 15 cc. of ether and brought to crystallization by addition of 5 cc. of petroleum ether. A yield of 4.2 g. (42%) of the acetylated dimethyl acetal was obtained readily. (2) A similar experiment employing the crystalline chloro derivative of rotation +52.5° yielded 4.4 g. (44%) of the same tetraacetyl-*d*-arabinose dimethyl acetal.

Tetraacetyl-*d*-arabinose dimethyl acetal crystallizes in prisms, melting at 80° (corr.) and showing a specific rotation of +21.8° in chloroform (*c*, 1.33). It is readily soluble in ether and chloroform, almost insoluble in water, and insoluble in petroleum ether. It does not reduce Fehling's solution.

Anal. Calcd. for $C_5H_6O_4(OCH_3)_2(COCH_3)_4$: C, 49.4; H, 6.6; OCH_3, 17.0; acetyl, 10.98 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.5; H, 6.7; OCH_3, 16.9; acetyl, 11.00 cc.

***d*-Arabinose Dimethyl Acetal.**—A solution of 6 g. of tetraacetyl *d*-arabinose dimethyl acetal in 120 cc. of absolute methyl alcohol was cooled to 0°, 0.4 cc. of 2 *N* barium methylate added, and allowed to stand at 0° for two hours. Upon volatilization of the solvent a crystalline residue of 3.3 g. (quantitative) rotating −16.8° in water was obtained, and recrystallization from 5 parts of methyl alcohol to constant rotation, yielded 2.8 g. (88%) of pure *d*-arabinose dimethyl acetal. This compound crystallizes in clear hexagonal prisms melting at 122° and showing a specific rotation of −18.5° in water. It does not reduce Fehling's solution, but upon hydrolysis at 98° in 0.05 *N* hydrochloric acid it yielded *d*-arabinose, and upon treatment with acid methyl alcohol it gave a mixture of methyl-*d*-arabinosides. We expect to study its change to glycosides in more detail later.

Anal. Calcd. for $C_5H_{10}O_4(OCH_3)_2$: C, 42.8; H, 8.2; OCH_3, 31.6. Found: C, 42.8; H, 8.2; OCH_3, 31.6.

Summary

Studies have been made of the action of catalyzed acetylating mixtures upon α and β methyl-*d*-arabinopyranoside triacetates. The results indicate: (1) that zinc chloride catalysis completely ruptures the lactonyl linkage without hydrolysis of the methyl group, to yield two isomeric pentaacetyl-*d*-arabinose methyl hemi-acetals; (2) that 0.16% sulfuric acid causes an equilibrium between a small amount of ring acetate and these hemi-acetals; and (3) that 4% sulfuric acid brings

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[6] Freudenberg, Hochstetter and Engels, *Ber.*, **58**, 668 (1925).

about a similar equilibrium followed by hydrolysis of the methyl group and peracetylation to yield aldehydo-*d*-arabinose hexaacetate.

The isomeric pentaacetyl-*d*-arabinose hemi-acetals have been converted to two isomeric chloro derivatives, which by the usual methods are converted into the same tetraacetyl-*d*-arabinose dimethyl acetal.

d-Arabinose dimethyl acetal has been synthesized in crystalline condition by deacetylation of its tetraacetate.

WASHINGTON, D. C. RECEIVED APRIL 23, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Densities and Vapor Pressures of Some Alkylbenzenes, Aliphatic Ketones and *n*-Amyl Chloride[1]

BY J. C. RINTELEN, JR., J. H. SAYLOR AND P. M. GROSS

During the course of an investigation of the solubility of some organic compounds being carried out in this Laboratory, it became necessary to know the vapor pressures and densities of these compounds at 10, 30 and 50°. An examination of the literature showed that there were no available density and vapor pressure data for some of the substances and that there were rather serious discrepancies in the vapor pressure data for ethylbenzene, the xylenes and mesitylene. Therefore, their vapor pressures together with the vapor pressures and densities of *n*-amyl chloride and some ketones were determined. After the experimental part of this work was completed, Kassel[2] called attention to the erroneous data of Woringer[3] for the vapor pressures of the xylenes and mesitylene that are given in the "International Critical Tables." Kassel redetermined the vapor pressures of these compounds.

Experimental

Materials.—The ethylbenzene and the dibutyl ketone were prepared in this Laboratory. The other substances were the best grades commercially available. All were subjected to a careful purification by successive fractionation using efficient stills and calibrated thermometers. Boiling points were corrected to 760 mm. by means of Craft's rule whenever the value of d*T*/d*P* could not be found in the literature. The boiling ranges of the samples used are given in Table I.

TABLE I

BOILING POINT RANGES OF THE COMPOUNDS

Substance	B. p. range, °C.	Previously observed b. p., °C.	Ref.
Ethylbenzene	136.13–136.18	136.15	4a
o-Xylene	144.0 –144.1	144.0	4b
m-Xylene	138.99–139.15	139.3 (139.00)	4b (6)
p-Xylene	138.27–138.37	138.4 (138.3)	5 (6)
Mesitylene	164.5 –164.6	164.6	4b
n-Amyl chloride	107.74–107.78	105.7 (106.6, 740 mm.)	6, (7)
Methyl isopropyl ketone	94.0 –94.52	95–96, 93–94, 95–95.3	8, 9, 10
Methyl isobutyl ketone	116.71–116.78	116.85	4c
Diethyl ketone	101.59–101.74	101.7	8
Dipropyl ketone	144.05–144.12	144.1	4b
Dibutyl ketone	187.4 –188.4	187.65	4d

Method.—The vapor pressures were measured by a differential static method. As the form of apparatus used has been found to be particularly convenient, it is shown in Fig. 1.

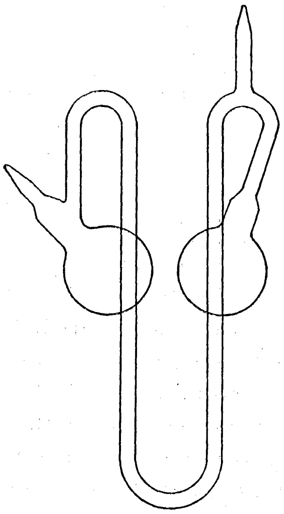

Fig. 1.—Vapor pressure apparatus.

Mercury was introduced into the manometer through the vertical tube, water placed in one bulb and the organic liquid in the other. The mercury in the manometer was

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[1] Taken in part from a thesis submitted by J. C. Rintelen, Jr., in partial fulfilment of the requirement for the degree of Doctor of Philosophy at Duke University, June, 1936.

(2) Kassel, THIS JOURNAL, **58**, 670 (1936).

(3) Woringer, *Z. physik. Chem.*, **34**, 257 (1900).

(4) (a) Timmermans, *Bull. soc. chim. Belg.*, **25**, 300 (1911); (b) **30**, 62 (1921); (c) **27**, 334 (1913); (d) **36**, 506 (1927).

(5) Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926).

(6) "International Critical Tables."

(7) Lieben and Rossi, *Ann.*, **159**, 72 (1871).

(8) Timmermans and Mattaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).

(9) Henderson, Henderson and Heilbron, *Ber.*, **47**, 887 (1914).

(10) Clarke, THIS JOURNAL, **33**, 528 (1911).

heated and the water and organic liquid in the bulbs were boiled. Then both sides of the apparatus were evacuated simultaneously while gentle heating continued for thirty minutes. The capillaries were then sealed off.

Temperatures were controlled by thermostats regulated to within ±0.02°. The difference in the mercury levels in the arms of the manometer was read with a cathetometer and corrected to 0°. This added to or subtracted from the vapor pressure of water at the temperature in question, gave the vapor pressure of the liquid. Each apparatus was set up in duplicate for each substance and readings made at 10, 30 and 50°. The method was checked by carrying out the procedure with water in both sides of the apparatus. Several trials gave an average deviation from zero of 0.1 mm.

The densities were determined with a 10-cc. specific gravity bottle, in the same thermostats. These determinations were also made in duplicate at 10, 30 and 50°.

Results

Table II gives a summary of the vapor pressure and density data. Each result is the average of two independent determinations. The duplicate vapor pressure determinations agreed within 0.6 mm. in most cases and the density determinations to within less than 1 part in 10,000.

TABLE II

VAPOR PRESSURE AND DENSITY DATA

Substance	Vapor pressures, mm. 10°	30°	50°	Densities, d_4^t, g./ml. 10°	30°	50°
Ethylbenzene	2.9	11.6	34.6			
o-Xylene	1.6	7.4	25.1			
m-Xylene	2.2	9.1	29.3			
p-Xylene	2.3	10.7	32.3			
Mesitylene	0.6	3.8	11.5			
n-Amyl chloride	15.0	41.2	100.8	0.8940	0.8750	0.8544
Methyl isopropyl ketone	27.4	67.3	166.7	.8239	.8052	.7847
Methyl butyl ketone				.8198	.8025	.7845
Methyl isobutyl ketone	8.0	26.2	70.1	.8094	.7922	.7736
Diethyl ketone	16.9	46.1	117			
Dipropyl ketone	3.0	9.5	25.6			
Dibutyl ketone	1.5	4.7	12.6	.8296	.8148	.7981

The constants of the equation $\log_{10} P = (A/T) + B$ have been determined from a plot of the data for those substances for which no other vapor pressure data is known. While the limitations of such equations based on a few points is, of course, realized, they are given for convenience in interpolation. In these equations 0°C. = 273.16°K. The values of the constants are given in Table III. The average deviation of the observed values from those calculated is less than 1% in all cases.

TABLE III

CONSTANTS FOR THE VAPOR PRESSURE EQUATIONS

Substance	$-A$	B
n-Amyl chloride	1892	7.8573
Diethyl ketone	1926	8.0236
Dipropyl ketone	2126	7.9864
Dibutyl ketone	2101	7.6031

Kassel's values are in fair agreement with our own results although they are usually higher. Kassel points out that the accuracy of his data is limited by the fact that he did not purify his substances. Whether the differences noted here arise because of this or because of a small systematic error in our method or in his is not clear.

The results of Woringer used in the "International Critical Tables" are obviously wrong with the possible exception of those for *m*-xylene. This is probably attributable to a systematic error in method or more likely to the use of impure materials as he reported determinations by the same method for other compounds such as benzene and toluene which agree fairly well with the well established data of others.

Values for the vapor pressures of the hydrocarbons at 0° are given by Linder.[11] When our values are extrapolated to 0°, they are found to agree well with his except in the case of *m*-xylene and *p*-xylene. Values for *m*-xylene at higher temperatures given by Kudryavtzev[12] check with our results. Values for the vapor pressures for ethylbenzene at higher temperatures given by Kurbatov[13] check fairly well with our results while those given by Vvendenski[14] do not.

The values of Mayberry and Aston[15] for the vapor pressures of methyl isopropyl ketone and methyl isobutyl ketone given in Table III are only in fair agreement with ours.

Summary

The vapor pressures of ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, *n*-amyl chloride, methyl isopropyl ketone, methyl isobutyl ketone, diethyl ketone, dipropyl ketone and dibutyl ketone have been determined at 10, 30 and 50°. The densities of *n*-amyl chloride, methyl isopropyl ketone, methyl butyl ketone, methyl isobutyl ketone and dibutyl ketone have been determined at 10, 30 and 50°.

DURHAM, N. C. RECEIVED MARCH 20, 1937

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[11] Linder, *J. Phys. Chem.*, **35**, 53 (1931).

[12] Kudryavtzev, *J. Gen. Chem.* (U. S. S. R.), **4**, 563 (1934).

[13] Kurbatov, *Leningrad Tech. Inst.*, **1**, 32 (1927).

[14] Vvendenski, *J. Gen. Chem.* (U. S. S. R.), **2**, 826 (1932).

[15] Mayberry and Aston, THIS JOURNAL, **56**, 2682 (1934).

An Improved Method of Purifying Europium*

BY HERBERT N. McCOY

WITH NOTES BY ARTHUR S. KING ON ITS "SPECTROSCOPIC PURITY," BY LINUS PAULING ON THE "ISOMORPHISM OF EUROPOUS SULFATE WITH STRONTIUM AND BARIUM SULFATES," AND BY G. P. BAXTER AND F. D. TUEMMLER ON THE "ATOMIC WEIGHT OF EUROPIUM"

The method described earlier[1-3] for the separation of europium from other rare earths leads easily to a fairly complete recovery of this element from monazite residues and gives, after a sufficient number of repetitions of the process, substantially pure europium. However, the material obtained after eight or nine successive precipitations as sulfate still contains a few tenths of a per cent. of impurities—principally neodymium, samarium and gadolinium. Doubtless any required degree of purity might be obtained by further repetitions of the process. The method though fast compared with fractional crystallization is rather laborious when the object is the preparation of material spectroscopically free from other rare earths.

The new process here described leaves little to be desired in the matter of speed, convenience and purity of product obtained. It depends upon the fact that a concentrated solution of europous chloride containing up to 30% of other rare earths gives with concentrated hydrochloric acid a crystalline precipitate of europous chloride dihydrate, $EuCl_2 \cdot 2H_2O$. This precipitate is practically free from other rare earths. By aid of this reaction in three days' time 125 g. of exceptionally pure europium oxalate was prepared. The progress of purification is shown by the following observations.

After one precipitation as europous chloride, no absorption bands of the other rare earths could be seen in a 10-cm. layer of the concentrated solution. The rare earths extracted from the filtrate showed strong bands of neodymium and weaker ones of samarium. After a second precipitation the rare earths from the filtrate showed in addition to europium only the strongest bands of neodymium (λ 5205 and λ 5522, and the group at λ 5726 to 5782) and these were very faint. After a third precipitation, europium recovered from the filtrate showed no bands of the other rare earths. The method is therefore very effective in the purification of europium. How effective was shown by an examination of its emission spectrum.

This work was kindly undertaken by Dr. Arthur S. King, who has made exhaustive studies of rare earth spectra.[4]

Dr. King states: "A spectrogram made with the 15 foot [454 cm.] concave grating having 15,000 lines to the inch [2.54 cm.] showed the sample of europium chloride to be of high purity. An examination of the ultraviolet region where many strong lines of gadolinium normally occur showed only faint traces of the strongest of these. One or two of the strongest lines of lanthanum may be present in this region. Barium and calcium are also present."

Following this examination, which showed traces of gadolinium present and probably lanthanum and by inference also some neodymium and samarium, the whole of the material was given two further precipitations (making a total of five) as europous chloride. A new sample in the form of trichloride was examined by Dr. King who reported: "The spectrogram of this new sample made with a normal exposure (for europium) showed no lines of other rare earths. The strongest lines of neodymium, samarium and gadolinium were looked for especially but not found."

"A second spectrogram, so much overexposed as to be useless for europium, showed three or four lines of neodymium, especially the strongest at λ 4303. No samarium or gadolinium lines could be seen on this plate. By comparison with plates exposed similarly and made with europium-neodymium mixtures of known composition, the amount of the latter present in the purest europium was estimated as not more than one in 100,000. Barium and calcium are still present in noticeable amounts."

Experimental Part

The starting material was a rare earth chloride solution of density 1.35. It had been partially purified by three successive precipitations as europous sulfate.[3] About 70% of its rare earth content was europium, the remainder being mostly neodymium, samarium and gadolinium. Four

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* This article consists of four independent papers on closely related subjects. Each supplements the others to round out a research that would have been impossible without coöperation. It is a great pleasure to acknowledge my indebtedness to my collaborators.

(1) McCoy, THIS JOURNAL, **57**, 1756 (1935).

(2) *Ibid.*, **58**, 1577 (1936).

(3) *Ibid.*, 2278 (1936).

(4) King, *Astrophys. J.*, **68**, 194 (1928); **72**, 221 (1930); **74**, 328 (1931); **75**, 40 (1932); **77**, 9 (1933).

hundred ml. of this chloride solution was put in a quart (liter) bottle[5] with a few ml. of concentrated hydrochloric acid and 100 g. of 30-mesh amalgamated C. P. zinc. The bottle, tightly stoppered, was shaken vigorously by hand and from time to time was placed directly before the slit of the spectroscope for the observation of the absorption spectrum of the solution. The latter, nearly colorless at first, turned yellowish and the europium band at λ 5253 gradually faded until after thirty or forty minutes it was no longer visible. All other absorption bands of europium had disappeared also, thus showing complete reduction.[2] The solution was next decanted from the remaining zinc into a second quart bottle in an atmosphere of carbon dioxide. The second bottle was closed by a two-holed stopper carrying a 250-ml. dropping funnel and a capillary outlet for the escape of gas. Concentrated hydrochloric acid was now run in slowly from the dropping funnel, while the contents of the bottle was kept well mixed. When about 200 ml. of acid had been added crystallization of hydrated europous chloride began and reached a maximum with about 500 ml. of acid. Ninety per cent. of the europium present separated out. The somewhat warm mixture was set in a refrigerator for two or three hours. It now consisted of nearly equal parts by volume of pure white crystals with a light blue fluorescence and an almost colorless mother liquor.

In filtering the crystals, which oxidize in air with great ease, a 12-cm. porcelain funnel with cotton filter cloth was used. It was fitted with a cardboard collar extending 12 to 15 cm. above the rim of the funnel. Carbon dioxide was led into the filter and collar in a rapid stream during filtration.[6] The crystals were not washed but were sucked as dry as possible.

With care, very little oxidation occurs. If oxidation takes place the filter cake gets very hot and fumes of hydrogen chloride come off. The cake of europous chloride was dissolved in water and the solution poured into a carbon dioxide filled bottle for repetition of the whole process. The second and following operations went much like the first, excepting that less time was required for the reduction as the material was mostly in the reduced state at the start.

After five repetitions of the process, the final europous solution was oxidized with nitric acid in the presence of sufficient hydrochloric acid to form the trichloride, filtered from a trace of insoluble matter—largely carbon left from the zinc dissolved—and precipitated with a solution of oxalic acid. The yield of oxalate from 400 ml. of original solution was 125 g. This was about half of the rare earth content of the starting material.

Subsequently three further lots of material were refined in this way. Five successive precipitations of each lot as europous chloride yielded a total of about 500 g. of pure europium oxalate.

The preparation of europous chloride dihydrate for analysis and its subsequent weighing was carried out wholly in an atmosphere of carbon dioxide since the substance oxidized rapidly on exposure to air. The chloride was made as already described, and filtered, washed, and weighed in a 130-ml. filtering tube having a coarse fritted glass filter plate.

The apparatus was arranged so that the tube could be kept filled with pure dry carbon dioxide (from "dry ice"). A 10% solution of hydrogen chloride in methyl alcohol, contained in an attached dropping funnel, was used for washing the europous chloride. The alcohol and excess hydrogen chloride were finally removed by a fast stream of carbon dioxide gas while the tube and its contents were gently warmed. When the outflowing gas no longer affected congo paper the material was free from excess acid and was dry.

The outlet of the filtering tube was now closed with a rubber plug and the stopper replaced by a solid rubber stopper. The tube and contents were weighed, the crystals, 1.9165 g., were dissolved in water and made up to 250 ml. Fifty-ml. portions were analyzed for europium and chlorine. The solution was oxidized with nitric acid and the europium precipitated as oxalate, ignited and weighed as oxide. The chloride was determined in a separate portion of solution as silver chloride.

0.3833 g. of substance gave 0.2619 g. of europium oxide and 0.4301 g. of silver chloride. Calcd. for $EuCl_2 \cdot 2H_2O$: Eu, 58.7; Cl, 27.4. Found: Eu, 59.0; Cl, 27.8.

The crystals of europous chloride dihydrate could not be distinguished under the microscope from those of barium chloride dihydrate which are similarly precipitated by hydrochloric acid. The two may be isomorphous.

The carrying down of europous sulfate with barium sulfate[7] and with strontium sulfate[8] suggests that these salts may also be isomorphous. In fact the possible isomorphism of strontium and europium sulfate led Brukl to use the former to carry down the latter in extracting 12 g. of europium from a rare earth mixture by an electrolytic method closely resembling that used by Yntema.[9]

Europous sulfate, like barium and strontium sulfates, is not hydrated and is almost insoluble in water. In acids it is but little soluble except when oxidation occurs. The density of europous sulfate was determined and was found to be still greater than those of barium and strontium sulfates.

These facts made it seem desirable to discover whether isomorphism plays a part in the similarities mentioned. Dr. Linus Pauling of the California Institute of Technology kindly offered to make the examination. As the method used was not well suited to a body so readily oxidized as europous chloride, the determinations were confined to the sulfates.

The density determinations of europous sulfate were made by the use of two auxiliary liquids—tetrachloroethane and benzene. The former led to a value of 4.981 at 25°, the latter to one of 4.989 at 20°.

Report on the X-Ray Study of the Isomorphism of Compounds of Bivalent Europium and Barium

BY LINUS PAULING

The X-ray powder photographs taken during this investigation were prepared with the use of

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[5] Quart milk bottles are admirably suited for this purpose and are superior to any of the usual chemical shapes.

[6] This was supplied by 300 to 400 g. of solid carbon dioxide in a liter flask.

[7] Selwood, THIS JOURNAL, **57**, 1145 (1935).

[8] Brukl, *Angew. Chem.*, **49**, 159 (1936).

[9] Yntema, THIS JOURNAL, **52**, 2782 (1930).

CuK α radiation (λ = 1.539 Å.) filtered through nickel. The camera radius was 5.00 cm. The crystal powder was mounted on the surface of a small glass fiber; a correction for absorption in the sample was applied.

Photographs of barium sulfate, europous sulfate, and a powder formed by precipitation of a solution containing equal mole fractions of europous chloride and barium chloride with sulfuric acid were found to be closely similar in appearance. The barium sulfate photographs could be indexed on the basis of the accepted orthorhombic unit with a_0 = 8.85 Å., b_0 = 5.44 Å., and c_0 = 7.13 Å. The europous sulfate photographs show lines corresponding to an orthorhombic unit with a_0 = 8.46 Å., b_0 = 5.37 Å., and c_0 = 6.90 Å. (all ± 0.02 Å., the errors being larger than usual because of uncertainty in the correction for absorption). The space group criteria for V_h^{16}, with the orientation Pnma as in barium sulfate, are satisfied, and the intensities of corresponding lines on the two photographs are about the same. This indicates strongly that the substances are isomorphous. Verification is provided by the photographs of the powder prepared by simultaneous precipitation of europous sulfate and barium sulfate, which shows instead of the lines of the two substances but a single pattern midway between them, proving that the powder is a solid solution of europous sulfate and barium sulfate.

The density calculated from the X-ray data for europous sulfate, assuming 4 $EuSO_4$ in the unit cell, is 5.22 g./cc., in approximate agreement with the directly determined value 4.99 g./cc.

The lattice constants of europous sulfate are intermediate between those of barium sulfate and those of strontium sulfate, which also has the barium sulfate structure:

	a_0, Å.	b_0, Å.	c_0, Å.
$BaSO_4$	8.85	5.44	7.13
$EuSO_4$	8.46	5.37	6.90
$SrSO_4$	8.36	5.36	6.84

Taking 1.35 Å. as the ionic radius (for coördination number 6) of Ba^{++} and 1.13 Å. as that of Sr^{++}, we interpolate to obtain 1.17 Å. as the ionic radius of Eu^{++}. It may be pointed out that this lies closer to the value for Sr^{++} than to that for Ba^{++}.

These results give a definite answer to the question of the isomorphism of europous sulfate with barium and strontium sulfates. It is thus plain why the last two salts are effective in aiding the precipitation of the first from dilute solutions.

A part of my best europium oxalate amounting to 190 g., essentially free from all rare earth impurities, but still contaminated with traces of calcium and barium, was sent to Dr. Gregory P. Baxter of Harvard University who kindly agreed to undertake a new determination of the atomic weight of europium. A preliminary report of the results obtained follows.

Report by G. P. Baxter and F. D. Tuemmler

A preliminary determination of the atomic weight of europium has been made by analysis of europous chloride. The original oxalate was ignited and after solution in nitric acid the europic nitrate was purified by several crystallizations from concentrated nitric acid. After two precipitations of europic oxalate in the presence of half normal acid, with conversion to oxide, the latter was dissolved in hydrochloric acid and europic chloride purified by crystallization from hydrochloric acid. Spectroscopic examination gave no evidence of the presence of barium or calcium.

Attempts to prepare anhydrous europic chloride by careful dehydration in dry hydrogen chloride even in the presence of high percentages of chlorine were uniformly unsuccessful. The product contained much europous chloride, even when not fused, while fusion accentuated the difficulty.

On the other hand, if the europic chloride is carefully dehydrated and fused in a current of hydrogen chloride and hydrogen, complete reduction to europous chloride is apparently attained, and the fused material remains essentially constant in weight in dry air.

Weighed quantities of europous chloride were dissolved and allowed to oxidize in the air, in the presence of a small excess of nitric acid to prevent the precipitation of basic salt. The solutions were then compared with solutions of weighed nearly equivalent amounts of pure silver by the equal opalescence method. Pending the determination of the density of the anhydrous europous chloride the value 5.00 is assumed for the computation of the vacuum correction. The following table gives the results so far obtained.

THE ATOMIC WEIGHT OF EUROPIUM

EuCl$_2$, g.	Ag, g.	Ratio EuCl$_2$:2Ag	At. wt. Eu
2.37131	2.29571	1.03293	151.95
3.08192	2.98364	1.03294	151.95
2.81855	2.72847	1.03301	151.97
4.88930	4.73350	1.03291	151.95
	Average	1.03295	151.95

Urbain and Lacombe [*Compt. rend.*, **138,** 627 (1904)] found 151.96; Jantsch [*ibid.*, **146,** 473 (1908)], 152.04; Aston [*Proc. Roy. Soc.* (London), **A146,** 46 (1934)] from the isotopic constitution, 151.90; Hopkins and Meyers [THIS JOURNAL, **57,** 241 (1935)], 152.30. The International value has been 152.0 for some time.

Summary

1. A concentrated solution of the chlorides of the rare earths containing 70% or more of europium gives upon reduction of the latter with zinc and treatment with concentrated hydrochloric acid a crystalline precipitate of europous chloride dihydrate, EuCl$_2$·2H$_2$O, practically free from accompanying rare earths.

2. By means of this reaction about 500 g. of europium oxalate has been prepared, the high purity of which is shown by spectrograms by Dr. King.

3. An X-ray examination by Dr. Pauling has established the isomorphism of EuSO$_4$ and BaSO$_4$, and therefore also of SrSO$_4$.

4. Dr. Baxter and Mr. Tuemmler have completed the purification of europium and determined its atomic weight to be 151.95.

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RECEIVED APRIL 24, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Raman Spectrum and the Structure of Water

BY PAUL C. CROSS, JOHN BURNHAM AND PHILIP A. LEIGHTON

The tridymite-like structure of ice as regards the distribution of the oxygen atoms appears to be definitely established,[1] and Pauling's[2] explanation of the discrepancy between the third law and statistical entropies in ice leaves little doubt that the hydrogens are unequally spaced between the oxygens. Each four-coördinated oxygen nucleus, at 0°, has bonded at tetrahedral angles four oxygens at d = 2.76 Å., with a proton along each oxygen–oxygen axis; two chemically bonded at d = 0.99 Å. (see section III) and two "hydrogen bonded" at d = 1.77 A. Present theory, as developed by Bernal and Fowler[3] and modified by Katzoff[4] and others, considers liquid water at ordinary temperatures as having essentially a broken down ice structure, with a considerable amount of coördination still persisting through hydrogen bonding which, however, decreases with increasing temperature or addition of electrolytes. Little progress has been made beyond this qualitative picture, and to obtain further evidence on the nature and extent of coördination in water the authors have reinvestigated, using rather high dispersion, the Raman spectrum of water over a wide range of temperatures, of ice at 0°, and of deuterium oxide. The results are treated on the basis of a model consisting of coupled O—H oscillators perturbed by various types of coördination.

An empirical treatment of the perturbation forces leads to an estimate of the intermolecular frequencies which confirms their identification. For earlier measurements and their interpretation we refer to the review and bibliography of Magat[5] and to the recent paper of Hibben.[6]

I. Experimental Data

The Raman spectra were excited by the unreversed 2536.52 Å. line of a mercury–argon discharge lamp and photographed on a quartz spectrograph of 3.5 Å./mm. dispersion at 2650 Å. The water was placed in a fused silica tube of 30 mm. diameter for the work below 100°, while at higher temperatures the high pressures (up to 218 atm. at 375°) necessitated the use of a smaller bore; a 4-mm. tube with 1.1-mm. walls being employed. For frequency measurements each spectrum was partially overlaid with an iron arc spectrum. Wave lengths were corrected to vacuum.

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(1) Barnes, *Proc. Roy. Soc.* (London), **A125,** 670 (1929).

(2) Pauling, THIS JOURNAL, **57,** 2680 (1935).

(3) Bernal and Fowler, *J. Chem. Phys.*, **1,** 515 (1933).

(4) Katzoff, *ibid.*, **2,** 841 (1934).

(5) Magat, *Ann. phys.*, **6,** 108 (1936).

(6) Hibben, *J. Chem. Phys.*, **5,** 166 (1937).

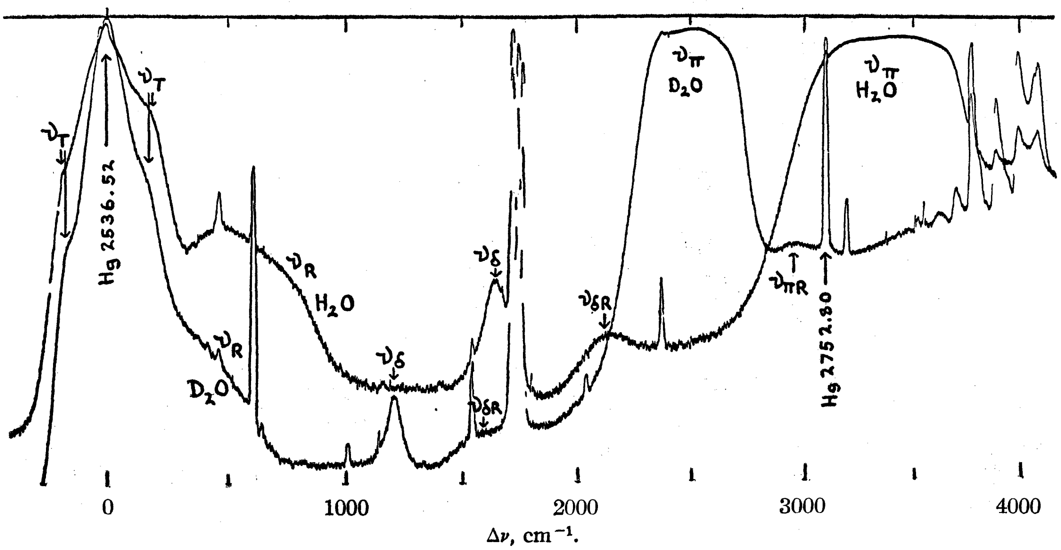

Fig. 1.—Comparison of the Raman spectra of H_2O (40°) and D_2O (50°).

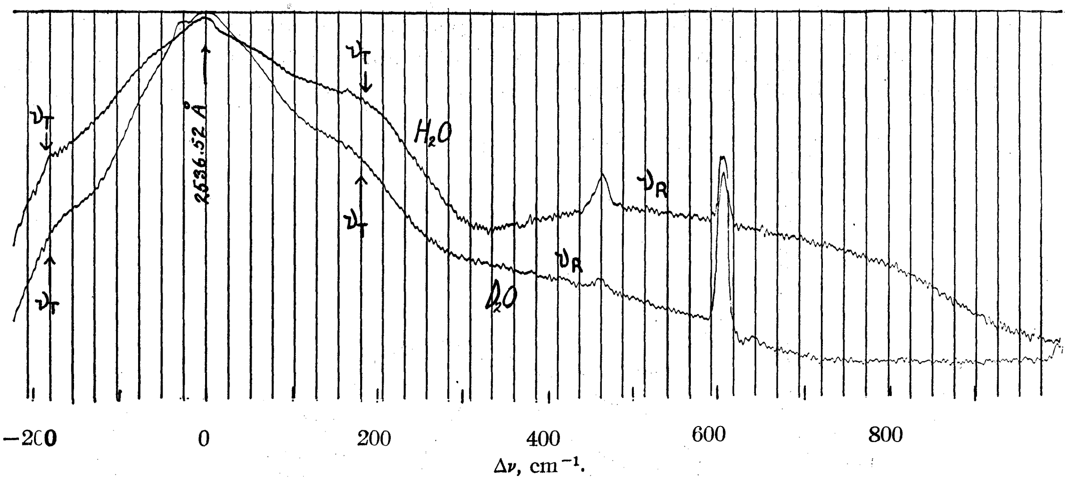

Fig. 2.—Low frequency Raman bands of H_2O (40°) and D_2O (50°).

In Fig. 1 are shown microphotometer records, obtained by use of the instrument described recently,[7] of the entire Raman spectrum of H_2O at 40° and D_2O at 50°. The main bands of each are overexposed in order to bring out the low frequencies. These low frequency bands are compared with greater linear magnification in Fig. 2, while in Fig. 3 the low frequency spectrum of melting ice at 0° is compared with that of water at 26 and at 80°. The exposures required to show these bands even to the small extent to which they appear in Fig. 3 were about twenty times greater than those required to give the main band the intensity shown in Figs. 4 and 5. Particularly noteworthy in Fig. 3 are the broadening in the neighborhood of the source line in liquid water as compared with ice; the sharp "hindered translation," ν_T, frequency in ice, observable both as a Stokes and anti-Stokes band; and the decrease in intensity of this frequency with increasing temperature in liquid water on the Stokes side as compared with its increasing intensity with increasing temperature on the anti-Stokes side. Frequencies of intensity maxima, taken from these figures, are given in Table I. Owing to the breadth and flatness of the ν_R (hindered rotation) band, which extends at least from 320 to 1020 cm.$^{-1}$ for H_2O and from 250 to 730 cm.$^{-1}$ for D_2O, no estimates of the maxima are attempted. The differences between the maxima of $\nu_{\delta R}$ and ν_δ are 511

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[7] Leighton, Smith and Henson, *Rev. Sci. Instruments*, **5**, 431 (1934).

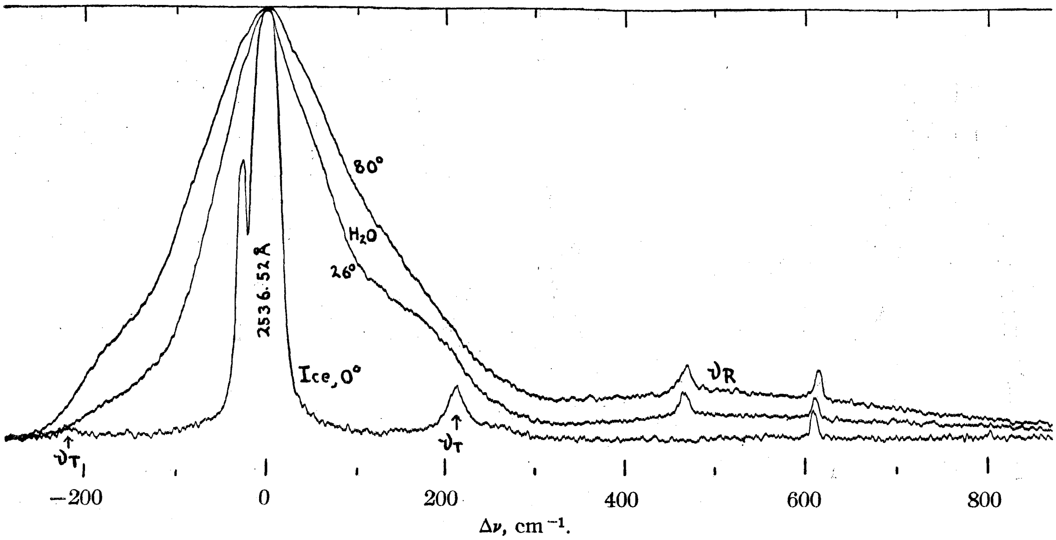

Fig. 3.—Low frequency Raman bands of ice at 0° and water at 26 and 80°.

and 392 cm.$^{-1}$ for H_2O and D_2O, respectively. All frequencies in D_2O, in accordance with theory, are approximately in the ratio of $2^{-1/2}$ to those in H_2O, with the exception of ν_T where the ratio, in agreement with the assignment of this frequency as a hindered translation, is $(20/18)^{-1/2}$.

The main band for melting ice at 0° is compared with that for water at two temperatures, 26 and 75°, in Fig. 4, and to facilitate comparison of shapes, the main bands of H_2O and D_2O at 40° are superimposed, using different frequency abscissas, in Fig. 5. The change in position and shape of the band with temperature in liquid water up to the critical temperature is shown in Fig. 6. The low intensity at 374° is due to an explosion of the cell before the exposure was completed, which shattered the discharge tube and terminated the experimental work. Although this band (as well as the ν_R band) is to be treated by a procedure which attaches minor significance to the precise positions of maximum intensity, such positions are recorded for reference in Fig. 7. Variations among different authors in the reported frequencies of the three apparent components,

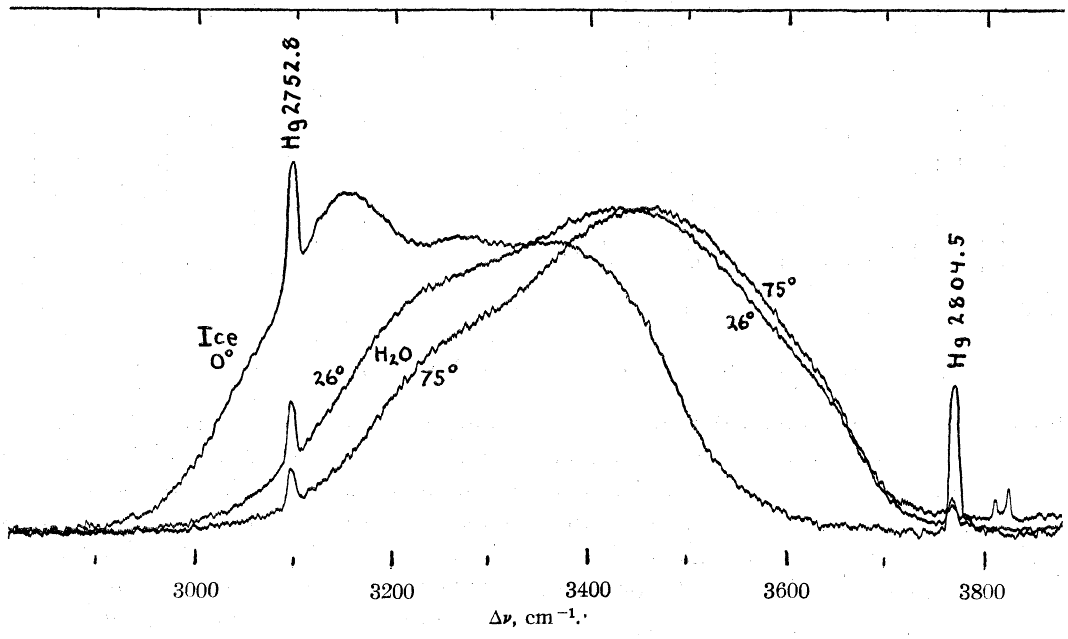

Fig. 4.—Main (ν_π) Raman band of ice at 0° and water at 26 and 75°.

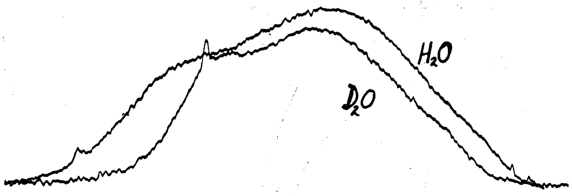

Fig. 5.—Main bands of H_2O and D_2O superimposed for comparison of shapes.

including the maximum, of the main band may be traced in part to temperature differences and in part to differences in the density of the photographic image obtained. The latter effect is illustrated in Fig. 8. Estimates, obtained from Figs. 4 and 8, of the positions of the principal components of the main band are given in Table II (notation from section II, 2).

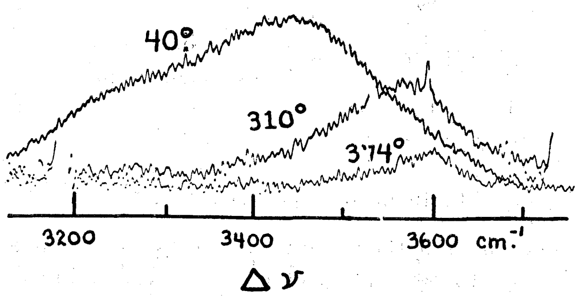

Fig. 6.—Shift in the main Raman band of water between 40° and the critical temperature.

TABLE I

FREQUENCIES OF INTENSITY MAXIMA

Band	Ice, 0°	H_2O, 40°	D_2O, 50°	Ratio ν_{D_2O}/ν_{H_2O}
ν_T	210 ± 2	200[a]	190[a]	0.95
ν_R	...	See Text		
ν_δ	...	1656 ± 2	1208 ± 2	.73
$\nu_{\delta R}$	...	2167 ± 5	1600[a]	.74
ν_π	3156 ± 3	3440 ± 5	2515 ± 5	.73
$\nu_{\pi R}$		4000[a]	2965 ± 5	.74

[a] No definite maximum; frequencies approximate.

II. Interpretation

1. The Hydrogen Bond and Coördination in Water.—The generally accepted theory of the structure of water is that formulated by Bernal and Fowler.[3] According to present views, the relatively open four-coördinated tridymite-like structure of ice is sufficiently broken down in liquid water to permit a closer packing of the water molecules than that in the ice crystal.

TABLE II

FREQUENCIES OF MAIN BAND COMPONENTS

Designation of component	Ice, 0°	Water, 40°	D_2O, 50°	Ratio ν_{D_2O}/ν_{H_2O}
$''\nu''_\pi$	3150	3190	2360	0.74
$'\nu''_\pi$	3270	..	..	
ν_π'' and $''\nu_\pi$	3390	3440	2515	.73
ν_π	..	3650	2680	.73

Although little definite information as to the extent of the coördination of liquid water has been published, it is generally implied that, in the range 0 to 100°, a high percentage (50–80%) of the maximum coördination still persists.

The coördination of water may be considered as due to the formation of hydrogen bonds between the oxygens. Pauling[2] has shown that two of the four hydrogens which tetrahedrally surround a four-coördinated oxygen atom are probably bonded to that oxygen in much the same manner as in an isolated water molecule, while the other two hydrogens are at a greater distance from the oxygen and essentially bonded to other oxygen atoms.

The energy of sublimation of ice, plus the knowledge that water is unassociated in the gas phase, permits an estimate of the energy of the hydrogen bond in water as very small, certainly less than about 6 kcal. per mole. This suggests that the intramolecular vibrations of a coördinated water molecule could be represented as perturbed vibrations of the isolated water molecule. The authors are indebted to Professor Linus Pauling for suggesting the simplified procedure for carrying out this treatment as outlined in the following paragraphs.

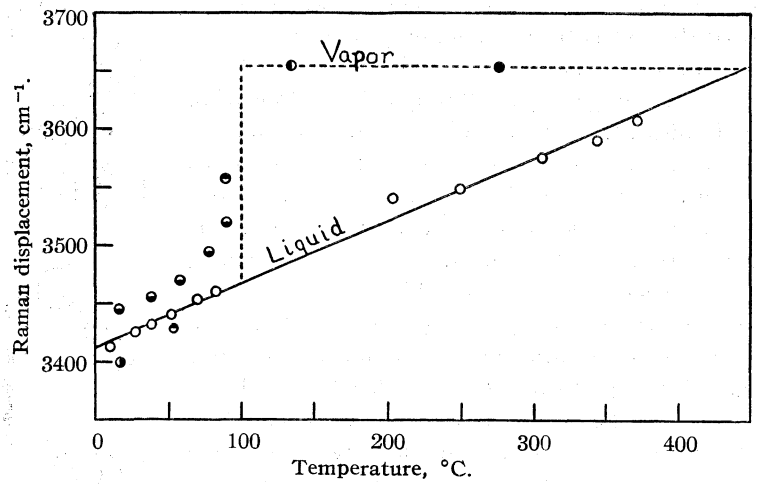

Fig. 7.—Frequency of maximum intensity in the main band (ν_π) as a function of temperature; ○, Authors; ◒, Specchia; ◓, Meyer; ◑, Magat; ◐, Bender; ●, Johnston.

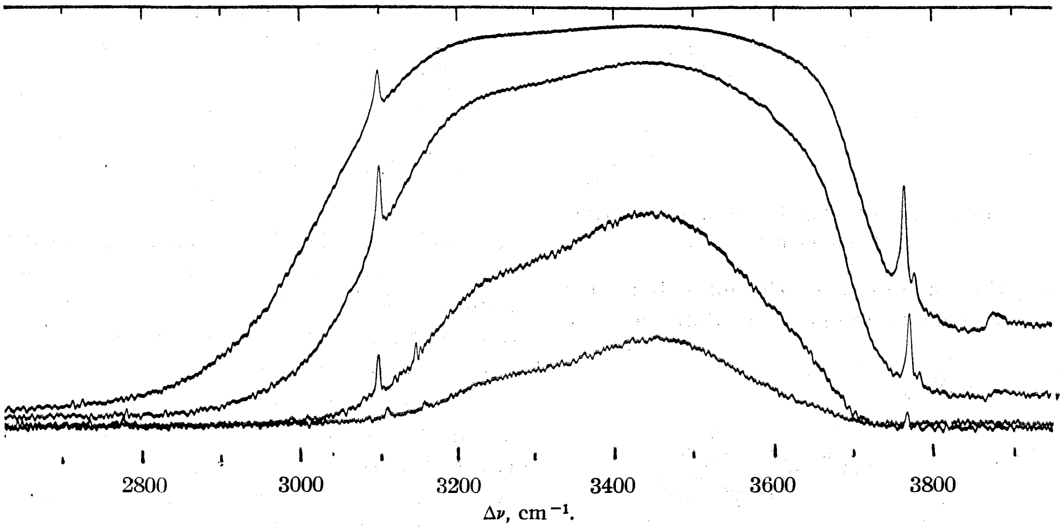

Fig. 8.—The main Raman band of water at 40°, as obtained with different times of exposure.

2. Model of Water Molecule for Perturbation Treatment.—By virtue of the large mass of the oxygen atom relative to the hydrogen atoms and the small value of the cross terms in the "valence force" representation of the potential energy of water, one may use as a satisfactory model for water, as far as the radial frequencies ν_σ and ν_π are concerned, simply two coupled O–H oscillators with a common oxygen atom, and each having a frequency ν_0.

A given water molecule has two possible types of perturbing hydrogen bonds:

I. Hydrogen bonds through the hydrogens of the molecule being considered. One may further assume that hydrogen bonds of this type perturb only the O–H oscillator of which the hydrogen is involved in the hydrogen bond, and that the perturbation is by an amount Δ cm.$^{-1}$, *i. e.*, ν_0 (perturbed) $= \nu_0 - \Delta$.

II. Hydrogen bonds through the hydrogens of molecules other than the one being considered. This type of perturbation may be assumed to affect equally both O–H oscillators by an amount δ cm.$^{-1}$. Furthermore, assuming that the interaction between the hydrogen bonds is negligible, two bonds of type II would shift the frequency of both O–H oscillators by 2δ cm.$^{-1}$. These two types of perturbation may combine to give nine varieties of perturbed water molecules, as shown in Fig. 9. The perturbation type is indicated by P with primes to the right for bonding through hydrogens of the molecule considered, type I, and primes to the left for bonding through hydrogens of neighboring molecules, type II. The secular equations and their solutions are given in equations (1) to (9). These equations are given in two groups, the first group of six including those which, according to our model, represent coupled identical oscillators and hence have symmetric and antisymmetric wave functions. The other three equa-

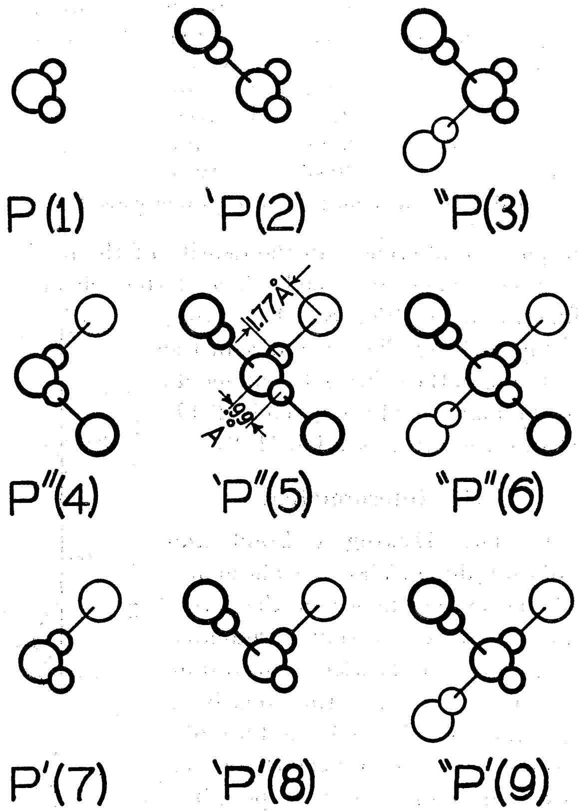

Fig. 9.—Types of coördinated water molecules, with numbers of the corresponding secular equations.

tions are for molecules having non-identical oscillators. Only approximate solutions are given for the latter.

Symmetrically Perturbed Types.—

$$\psi_A = \psi_\sigma = 2^{-1/2}\,\psi_1 - 2^{-1/2}\,\psi_2 \text{ and }$$
$$\psi_S = \psi_\pi = 2^{-1/2}\,\psi_1 + 2^{-1/2}\,\psi_2$$

(ψ_1 and ψ_2 refer to the wave functions of the respective OH oscillators, ψ_1 and ψ_2 refer to the antisymmetric combination, while ψ_S and ψ_π refer to the symmetric combination. ϵ is the coupling coefficient.)

$$\text{P,} \quad \begin{vmatrix} \nu - \nu_0 & \epsilon \\ \epsilon & \nu - \nu_0 \end{vmatrix} = 0 \qquad (1)$$
$$\nu_\sigma = \nu_0 + \epsilon,\ \nu_\pi = \nu_0 - \epsilon$$

$$\text{'P,} \quad \begin{vmatrix} \nu - \nu_0 + \delta & \epsilon \\ \epsilon & \nu - \nu_0 + \delta \end{vmatrix} = 0 \qquad (2)$$
$$\nu_\sigma = \nu_0 - \delta + \epsilon,\ \nu_\pi = \nu_0 - \delta - \epsilon$$

$$\text{''P,} \quad \begin{vmatrix} \nu - \nu_0 + 2\delta & \epsilon \\ \epsilon & \nu - \nu_0 + 2\delta \end{vmatrix} = 0 \qquad (3)$$
$$\nu_\sigma = \nu_0 - 2\delta + \epsilon,\ \nu_\pi = \nu_0 - 2\delta - \epsilon$$

$$\text{P}'', \quad \begin{vmatrix} \nu - \nu_0 + \Delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta \end{vmatrix} = 0 \qquad (4)$$
$$\nu_\sigma = \nu_0 - \Delta + \epsilon,\ \nu_\pi = \nu_0 - \Delta - \epsilon$$

$$\text{'P}'', \quad \begin{vmatrix} \nu - \nu_0 + \Delta + \delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta + \delta \end{vmatrix} = 0 \qquad (5)$$
$$\nu_\sigma = \nu_0 - \Delta - \delta + \epsilon,\ \nu_\pi = \nu_0 - \Delta - \delta - \epsilon$$

$$\text{''P}'', \quad \begin{vmatrix} \nu - \nu_0 + \Delta + 2\delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta + 2\delta \end{vmatrix} = 0 \qquad (6)$$
$$\nu_\sigma = \nu_0 - \Delta - 2\delta + \epsilon,\ \nu_\pi = \nu_0 - \Delta - 2\delta - \epsilon$$

Unsymmetrically Perturbed Types.—

$$\psi_{\text{I}} = \frac{\Delta}{(\Delta^2 + \epsilon^2)^{1/2}}\,\psi_1 - \frac{\epsilon}{(\Delta^2 + \epsilon^2)^{1/2}}\,\psi_2$$
$$= \frac{\Delta + \epsilon}{(2\Delta^2 + 2\epsilon^2)^{1/2}}\,\psi_\sigma + \frac{\Delta - \epsilon}{(2\Delta^2 + 2\epsilon^2)^{1/2}}\,\psi_\pi$$
$$\psi_{\text{II}} = \frac{\epsilon}{(\Delta^2 + \epsilon^2)^{1/2}}\,\psi_1 + \frac{\Delta}{(\Delta^2 + \epsilon^2)^{1/2}}\,\psi_2$$
$$= \frac{\epsilon - \Delta}{(2\Delta^2 + 2\epsilon^2)^{1/2}}\,\psi_0 + \frac{\epsilon + \Delta}{(2\Delta^2 + 2\epsilon^2)^{1/2}}\,\psi_\pi$$

$$\text{P}', \quad \begin{vmatrix} \nu - \nu_0 & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta \end{vmatrix} = 0 \qquad (7)$$
$$\nu_{\text{I}} = \nu_0 + \epsilon^2/\Delta,\ \nu_{\text{II}} = \nu_0 - \Delta - \epsilon^2/\Delta$$

$$\text{'P}' \quad \begin{vmatrix} \nu - \nu_0 + \delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta + \delta \end{vmatrix} = 0 \qquad (8)$$
$$\nu_{\text{I}} = \nu_0 - \delta + \epsilon^2/\Delta,\ \nu_{\text{II}} = \nu_0 - \Delta - \delta - \epsilon^2/\Delta$$

$$\text{''P}', \quad \begin{vmatrix} \nu - \nu_0 + 2\delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta + 2\delta \end{vmatrix} = 0 \qquad (9)$$
$$\nu_{\text{I}} = \nu_0 - 2\delta + \epsilon^2/\Delta,\ \nu_{\text{II}} = \nu_0 - \Delta - 2\delta - \epsilon^2/\Delta$$

3. Numerical Results.—Before attempting an identification of the component frequencies of the main band in the Raman spectrum of water, one must accept certain views concerning the identification of the unperturbed frequencies in this region.

It is generally admitted that the 3654 cm.$^{-1}$ Raman band of water vapor corresponds to the symmetric or ν_π vibration. This appears to disagree with Mecke's analysis of the infrared spectrum, which suggests that ν_π should have a frequency of about 3600 cm.$^{-1}$.[8] Inasmuch as this treatment gives at best only an approximation to the frequency changes, the absolute values of the frequencies used are not of prime importance. Accordingly, we somewhat arbitrarily select $\nu_\sigma = 3750$ cm.$^{-1}$ and $\nu_\pi = 3650$ cm.$^{-1}$, the observed fundamental frequencies from the infrared and Raman spectra, respectively. This is largely a matter of convenience in that it enables direct comparison of calculated and observed values without any intermediate and uncertain extrapolation to frequencies at infinitesimal amplitude. An additional factor aids in the simplification of the comparison with experimental data, namely, the Raman scattering can be taken as nearly completely due to the excitation of the symmetric vibrations. Thus, in our calculations to follow, the Raman spectrum will be compared to the envelope of the frequencies having wave functions $\psi = a\psi_\pi + b\psi_\sigma$ in which $a \neq 0$. Similarly our results may be compared with infrared measurements on liquid water by considering the frequencies for which $b \neq 0$.[9]

Substituting the above values for ν_σ and ν_π in the equation for the unperturbed molecule gives $\nu_0 = 3700$ cm.$^{-1}$ and $\epsilon = 50$ cm.$^{-1}$. Assuming that the low frequency hump in ice, Fig. 4, is the ν_π vibration of the four-coördinated structure,

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(8) Mecke, *et al.*, *Z. Physik*, **81**, 313, 445, 465 (1933). It is possible that this disagreement is only apparent and that the difference is due to an unanticipated peculiarity in the intensity pattern of the accompanying rotational transitions of the Raman band. However, the authors do not subscribe to the exceedingly simple structure of the Raman band proposed by Rank, Larsen and Bordner [*J. Chem. Phys.*, **2**, 464 (1934)]. A similar explanation is necessary to account for ν^δ occurring at 1648 cm.$^{-1}$ [Johnston and Walker, *Phys. Rev.*, **39**, 535 (1932)] in the Raman effect, whereas Mecke gives 1595 cm.$^{-1}$ as the center of the infrared band. The frequency ν_σ is so weak as to be unobserved in the Raman spectrum unless one assigns it to Rank's band at 3804 cm.$^{-1}$, which is again about 50 cm.$^{-1}$ higher than Mecke gives from the infrared. Bender [*ibid.*, **47**, 252 (1935)], however, points out that the Raman band of D_2O falls approximately where it is expected from Mecke's analysis, and accordingly holds that the discrepancy can hardly be due to a peculiarity in the intensities of the rotational lines in water. Furthermore, Bender measures the band as only about 10 cm.$^{-1}$ wide, which favors its interpretation as being a *Q* branch. If so, the vibrational frequency should be slightly above 3654 cm.$^{-1}$ rather than much below.

(9) This comparison will be exceedingly difficult because liquid water absorbs so strongly that this region appears in infrared measurements as a band nearly a thousand wave numbers wide with only 0.02 mm. of liquid in the light path [Gordy, *J. Chem. Phys.*, **4**, 769 (1936)] and the maximum is probably shifted by an unsymmetrical enhancement of the wings. The shift of the Raman maximum to lower frequencies with increasing exposure, shown in Fig. 8, supports this view that the apparent maximum of the infrared absorption would shift to higher frequencies if measurements were made with still thinner absorbing layers. Infrared absorption in this region may be further complicated by the contributions of $2\nu_\delta$, the first overtone of the bending frequency.

and taking its maximum as 3150 cm.$^{-1}$, one obtains from equation (6)

$$\Delta + 2\delta = 500 \text{ cm.}^{-1} \qquad (10)$$

A study of the envelope produced by various selections of Δ and δ which satisfy equation (10) led to the final choice of Δ = 250 cm.$^{-1}$ and δ = 125 cm.$^{-1}$. This yields the frequency patterns shown in Fig. 10. Strictly speaking, these patterns for the water spectrum are valid only at or near 0°, because the values of Δ and δ change with increasing temperature due to the increasing distance between the oxygen atoms and the corresponding weakening of the perturbation forces. To compare these calculated frequencies with the experimental intensities of scattering at various temperatures, one must make allowances for two variable factors: first, the distribution of the molecules among the various perturbation types; and, second, the shift of the frequencies themselves due to variations of the magnitude of the perturbing forces. These factors lead one to predictions of the nature of the changes in the main band with increasing temperature which are confirmed by the experimental results.

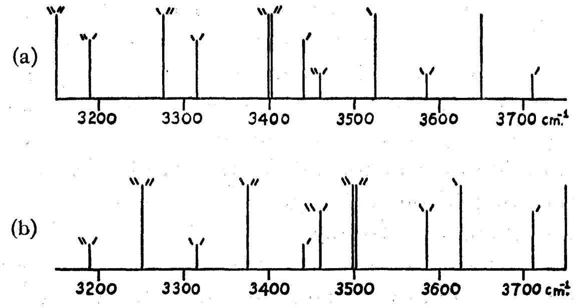

Fig. 10.—Calculated frequency patterns at 0°: (a) strong Raman components. Height of line proportional to a^2 ($\psi = a\psi_\pi + b\psi_\sigma$). (b) Strong infrared components. Height of line proportional to b^2 ($\psi = a\psi_\pi + b\psi_\sigma$).

Consider first the spectrum of ice. As expected, an intense maximum occurs at 3150 cm.$^{-1}$, due to four-coördinated water molecules. However, our picture shows maxima of unexpectedly high intensity at 3270 and 3390 cm.$^{-1}$, which should be assigned to three-coördinated and two-coördinated structures, respectively (see Table II).

If our interpretation is correct, this means that in ice which has been stored under conditions which permit slow melting, several per cent. of the molecules do not show the maximum coördination. Our experiment on ice is not conclusive since the ice was melting rapidly during the exposure, but we interpret the weakness of the scattering near 3600 cm.$^{-1}$ as an indication of relatively little contribution from water. Sutherland's[10] results on ice at −183° are in excellent accord with the idea that there is practically complete four-coördination at that temperature, giving a very sharp maximum at 3090 cm.$^{-1}$, 60 cm.$^{-1}$ below the corresponding maximum of our spectrum at 0° due to the temperature shift of the component "ν_π", which we estimate as about 3150 cm.$^{-1}$. More experiments on ice at and below 0° are very desirable before any definite statements regarding the deviation from complete four-coördination can be made. Our evidence is that hydrogen bonds are being broken before ice melts, and that it is probable that two-coördinated structures are slightly favored over three-coördinated structures,[11] an observation made necessary by the high intensity of the 3390 cm.$^{-1}$ component relative to the 3270 cm.$^{-1}$ component. The latter statement is, of course, based upon the assumption that the perturbations have no appreciable effect upon the intensity of Raman scattering.

When considering the main band of water at 26°, we have to permit a shift of the frequency pattern of Fig. 10 toward 3650 cm.$^{-1}$ by roughly 10% of the difference between 3650 and each component frequency. This gives the four-coördinated maximum at 3200 cm.$^{-1}$ to account for the hump observed at 3190 cm.$^{-1}$. The double frequency corresponding to the two types of symmetrical two-coördination would occur at 3425 cm.$^{-1}$ and account chiefly for the intense maximum of the Raman band at 3440 cm.$^{-1}$. Also, the slight indication of a high frequency component can be attributed to some free water molecules. We make no effort to observe regions specifically assigned to the unsymmetrically perturbed types because their number and lower intensity probably result in their contribution being more or less like a continuous background. The distribution of the molecules among the various perturbation structures has changed so that two-coördination is dominant. It appears from the Raman band intensities that water at 26° averages slightly more than two hydrogen bonds per molecule. Continuing the above considerations

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(10) Sutherland, *Proc. Roy. Soc.* (London), **A141**, 535 (1933).

(11) This result may be expected because the entropy of the two-coördinated structures will be considerably larger than that of the three-coördinated structures on account of the low-frequency pendulum-like oscillation which is introduced on forming the former from the latter.

to higher temperatures one can nicely account for all the features of the observed spectrum. We thus agree with Rao[12] that there are three components of the band (our ${}''\nu_\pi''$, ν_π'' and ${}''\nu_\pi$ together, and ν_π) which are observable above the background, but we admit many other indistinguishable components, and we consider the component frequencies as well as their intensities to shift with temperature. Needless to say, the considerations upon which our treatment is based attach little or no significance to the existence of definite polymolecular structures such as $(H_2O)_2$, $(H_2O)_3$, etc., so frequently postulated to account for the components of the main band in liquid water.

The measurements near the critical temperature probably represent scattering predominantly due to single water molecules. The slight shift from 3650 may be accounted for by some coördination, or it may be due to factors which we have neglected, especially since these experiments were made at such high pressures (> 200 atmospheres).

The structure of the main band of heavy water readily may be seen to conform to the same interpretation as that of ordinary water. All the frequencies are roughly in the ratio of $2^{-1/2}/$ to those of ordinary water, and the band is correspondingly narrower, as clearly evidenced by Fig. 5. The relatively greater intensity of the ${}''\nu_\pi''$ component in liquid D_2O, indicating relatively more four-coördination as compared with H_2O, is in conformity with other properties indicating higher coördination, *e. g.*, the higher temperature of maximum density, the sharper maxima in x-ray scattering, and the fact that the relative magnetic susceptibility of D_2O liquid/D_2O solid is less than that of H_2O liquid/H_2O solid.

III. Representation of the Perturbation Forces

In the preceding paragraphs perturbations have been invoked to obtain the effective displacements of the vibration frequencies of the water molecule necessary to explain the observed Raman spectrum. In this section it is proposed to give briefly some empirical calculations designed to represent semiquantitatively the perturbation forces. The results will be used later in the discussion of the low frequency bands of liquid water and heavy water.

The simplest function which gives a fair representation of the forces and energies accompanying bond formation as a function of the nuclear separation, r, of the atoms forming the bond is the well-known Morse function

$$V = D(1 - e^{a(r_0 - r)})^2 - D \qquad (11)$$

where D is the dissociation energy of the bond, r_0 the equilibrium separation of the nuclei, and a is a constant related to the vibration frequency of the bond. ($2Da^2 = 4\pi^2c^2\mu\nu^2 = k$, the force constant in the harmonic approximation to the vibration.) Assuming the uncoupled O–H oscillator of the preceding section to have a dissociation energy of one-half that of the water molecule, an equilibrium nuclear separation the same as the O–H separation in the normal state of the water molecule, and a vibration frequency of 3700 cm.$^{-1}$, one obtains the Morse function

$$V_{\text{O—H}} = 110(1 - e^{2.23(0.97-r)})^2 - 110 \qquad \text{(kcal. per mole)} \quad (12)$$

Since the "hydrogen bond" is also formed between hydrogen and oxygen atoms, it may further be assumed that its energy is represented by a function of the type

$$V_{\text{H---O}} = \beta V_{\text{O-H}} = 110\beta(1 - e^{2.23(0.97-r)})^2 - 110\beta \quad (13)$$

with β to be determined from some experimentally measured property of the bond. Selecting as that experimental property the perturbation of the vibration frequency, Δ, due to hydrogen bonding through the hydrogen of the oscillator being considered, β may be determined as a function of the distance between the oxygens.

Combining the two functions represented by equations (12) and (13) to represent the energy of the hydrogen in the hydrogen bond O—H---O as a function of the distance r from the oxygen to which the hydrogen is chemically bonded, and taking the O–O separation, d_0 = 2.76 Å. at 0°, one obtains

$$\begin{aligned} V_{\text{O—H---O}} = {} & -2De^{a(r_0-r)} + De^{2a(r_0-r)} \\ & -2\beta De^{a(r_0-d_0+r)} + \beta De^{2a(r_0-d_0+r)} \qquad (14) \\ = {} & -1910e^{-2.23r} + 8320e^{-4.46r} \\ & - 4.06\beta e^{2.23r} + 0.0375\beta e^{4.46r} \end{aligned}$$

Expanding this function in the vicinity of $r = r_0$ one may determine r'_0, the perturbed O–H distance at equilibrium, and β by the restrictions that the linear term must vanish at r'_0, and the quadratic term must give the proper force constant $k = 4\pi^2c^2\mu(\nu_0 - \Delta)^2$. The results are β = 0.25 and $r'_0 = 0.98_6$ Å.

IV. Calculation of the Intermolecular Frequencies and Other Properties

The potential function $V_{\text{O—H---O}}$ of equation (14), with the value of β = 0.25 just determined,

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[12] Rao, *Proc. Roy. Soc.* (London), **145**, 489 (1934).

may be used to calculate various other properties of the hydrogen bond. It must be understood that the use of such simple representations of the inherently complicated interactions of chemical bond formation can at best lead to results that are only qualitative.

1. The Shift of the Component Frequencies in the Main Band with Temperature.—The shift of the frequencies contributing to the main band may readily be determined as a function of d_0, the O–O separation, with the assumption that $\Delta = 2\delta$. Thus, from the density of ice, $d_0 = 2.76$ Å. at 0° and 2.735 Å. at −183°, and we may estimate the frequency of the main component of ice (“ν_π”) to shift toward lower frequencies by 30 cm.$^{-1}$ on cooling from 0 to −183°. This is in satisfactory agreement with the observed shift of 60 cm.$^{-1}$, from the frequency of maximum intensity of ice at 0°, 3150 cm.$^{-1}$, to Sutherland's value of 3090 cm.$^{-1}$ at −183°. Our value at 0° is undoubtedly high due to the overlapping of components of higher frequency, causing the maximum to shift upward from the true value of “ν_π”.

Determinations of the observed frequency shifts with temperature in the liquid state are very difficult because no one perturbation type predominates, as in ice, and because the changing distribution of types masks the effect of frequency shift. The large shift which we postulated in order to account for the observed main band of water at 26° (*e. g.*, Δ “ν_π” = 50 cm.$^{-1}$) indicates either that there is an abrupt increase of the O–O distance in the coördinated bond on melting or, more likely, that our function represents too small a change in frequency with O–O separation. The qualitative facts, both theoretical and experimental, are that the components of the main band are all shifted toward higher frequencies with increasing temperature (excepting the unperturbed ν_π, which, to our approximation, remains constant).

2. The Frequency of "Hindered Rotation."—As we pointed out in discussing the experimental results, the region from 320 to 1020 cm.$^{-1}$ represents an appearance of continuous scattering, and measurements of the "maximum" have little significance. Its structure is even more complicated than that of the main band, since most of the nine types of perturbed molecules have ratios of restoring force/moment of inertia which vary with the axis of rotation. The absence of any sufficiently strong components to be evident above the continuous background renders impractical any attempt to treat this band in the same manner in which the main band was treated.

Only one type of associated molecule, P″, lends itself to a convenient calculation of the frequency of hindered rotation from our potential function. In this case, bonds of type II (through hydrogens of neighboring molecules) are absent and no uncertain estimate of their directive forces is necessary. Justifiable approximations which simplify the calculation of the hindered rotation frequency of P″ molecules due to the hydrogen bonding of type I are:

(a) The center of rotation is taken at the oxygen atom.

(b) The O–H chemical bond is considered rigid, $r'_0 = 0.99$ Å.

(c) The force acting on the hydrogen is obtained from the linear term of the potential function $V_{\text{H---O}}$, which represents the energy of the hydrogen as a function of the distance from the oxygen of the neighboring hydrogen-bonded water molecule.

$$V'_{\text{H---O}}\,(r'_0) = 2a\beta D[-e^{a(r_0-d_0+r_0')} + e^{2a(r_0-d_0+r'_0)}] \quad (15)$$

(d) The force restoring the rotated O–H bond to its equilibrium orientation is the component of the above force along the tangent to the arc of motion of the hydrogen atom.

(e) The force constant, $k = 4\pi^2c^2\mu\nu^2$, for the calculation of the frequency (in cm.$^{-1}$) is obtained from the quadratic term of the expansion of the integral of the restoring force as a function of the displacement of the hydrogen atom along the arc of motion. μ may be taken as the mass of the hydrogen atom.

(f) The frequency of hindered rotation of the P″ molecule is independent of the axis of rotation and is equal to the frequency of oscillation of a single hydrogen-bonded hydrogen perpendicular to the line joining the oxygens. This holds for our approximation because the forces on the hydrogens act from points on the extended equilibrium bond directions.

From these considerations the frequency of hindered rotation, for infinitesimal amplitude, becomes

$$\nu = (2\pi c)^{-1}\,(1.56\,V'_{\text{H---O}}\,(r_0')/r_0'\mu)^{1/2} \sim 570 \text{ cm.}^{-1} \quad (16)$$

This falls very nearly in the center of the region described as due to "hindered rotation." If the potential function represents these restoring forces accurately, this result requires that the type II bonds do exert an appreciable directive action in order to account for the existence of scattering up to *ca.* 1020 cm.$^{-1}$. Others have postulated a combination frequency of hindered rotation and hindered translation (see following paragraph) to account for scattering around 700 cm.$^{-1}$, but we consider this unnecessary. Our view is supported by the fact that the upper limits of scattering for D_2O and H_2O are in approximately the ratio of $730/1020 = 0.715 \sim 2^{-1/2}$, whereas a combination of hindered rotation and hindered translation would have an upper limit with a ratio considerably greater than $2^{-1/2}$ (due to the larger ratio of the hindered translation frequencies of D_2O and H_2O $(20/18)^{-1/2}$). Our results indicate that the "hindered rotation" frequency of water molecules in the ice crystal should be of the order of 700 to 900 cm.$^{-1}$, considerably higher than that calculated by Bernal and Tamm.[13] Hibben's recent article[6] indicates that the scattering of ice in this region shows a considerable drop in intensity from that of water on the low frequency side, while the intensity of the high frequency side is enhanced. It is likely that the maximum of the entire region is not far from the component due to P″ type molecules, while the band variously reported to exist between 700 and 800 cm.$^{-1}$, and noticeable as a component near 800 cm.$^{-1}$ on Hibben's microphotometer record for ice, may be due to the contribution of the "P" type molecules.

3. The Frequency of Hindered Translation.—It has recently been suggested that much of the low frequency scattering of liquids is due to hindered translational oscillations rather than to rotational scattering.[14] In the case of water, it is quite certain that hindered translation is largely responsible for the observed scattering near 200 cm.$^{-1}$. This scattering is the water analog of the ice line at 210 cm.$^{-1}$. Here again we see the possibility of a very complex structure in the actual scattering spectrum. However, at this low frequency range, the absolute separation of the components with large relative separation may be too small to be noticeable under ordinary dispersion, hence the apparent sharpness of the ice line in spite of our previous conclusion that there were appreciable amounts of three- and two-coördinated molecules present during the time of our exposure.

The frequency of oscillation of a water molecule about its equilibrium position in the ice lattice may be estimated by an empirical treatment similar to that used in the previous calculations. Here again some assumptions are necessary to give reasonably simple equations.

(a) The O–H chemical bond is considered rigid, $r'_0 = 0.99$ Å.

(b) The energy of the hydrogen bond as a function of the O–O distance, d, is represented by the potential function

$$V_{\mathrm{O}\text{---}\mathrm{O}} = -55e^{2.23(1.96-d)} + 27.5e^{4.46(1.96-d)} \\ -2\gamma Ee^{b(s_0-d)} + \gamma Ee^{2b(s_0-d)} \qquad (17)$$

where the first two terms are from the function $V_{\mathrm{H}\text{---}\mathrm{O}}$ of section III as a function of d, with $\beta = {}^1/_4$, and the last two terms represent an O–O Morse function with an arbitary coefficient γ, to be determined from the equilibrium position $d_0 = 2.76$ Å. (at 0°). A closer examination of the last two terms in Equation (17) reveals that in the vicinity of $d_0 = 2.76$ Å., d is so large relative to $s_0 \sim 1.32$ Å.[15] that the final term may be ignored and the O–O repulsion represented by $-2\gamma\cdot Ee^{bs_0}\cdot e^{-bd}$. Furthermore, since γ is an arbitrary multiplier, $-2\gamma Ee^{bs_0}$ may be set equal to an arbitrary multiplier γ', and the Morse function representation of the oxygen–oxygen repulsion reduces, for our purpose, to the simple exponential form, $\gamma e'^{-bd}$, giving

$$V_{\mathrm{O}\text{---}\mathrm{O}}(d) = -4351e^{-2.23d} + 172100e^{-4.46d} + \gamma' e^{-bd} \qquad (18)$$

$$V_{\mathrm{O}\text{---}\mathrm{O}}(d_0) = -8.47 + \gamma' e^{-bd_0} = -D_{\mathrm{OHO}} \quad \text{(kcal. per mole)} \qquad (19)$$

$$V'_{\mathrm{O}\text{---}\mathrm{O}}(d) = 9703e^{-2.23d} - 767600e^{-4.46d} - b\gamma' e^{-bd} \qquad (20)$$

$$V'_{\mathrm{O}\text{---}\mathrm{O}}(d_0) = 17.1 - b\gamma' e^{-bd} \qquad (21)$$

$$V''_{\mathrm{O}\text{---}\mathrm{O}}(d) = -21640e^{-2.23d} + 3424000e^{-4.46d} + b^2\gamma' e^{-bd} \qquad (22)$$

$$V''_{\mathrm{O}\text{---}\mathrm{O}}(d_0) = -30.5 + b^2\gamma' e^{-bd_0} = k_{\mathrm{OO}} \quad \text{(kcal. per mole per Å.}^2\text{)} \qquad (23)$$

D_{OHO} is the dissociation energy of the hydrogen bond and k_{OO} is the force constant for the harmonic approximation to the vibration frequency of the hydrogen-bonded water molecules against each other. Various estimates of b are given below.

(c) Since definite information is lacking as to the type of vibrational motion concerned in the Raman excitation of the 210 cm.$^{-1}$ frequency of ice, the following calculations are made for two different assumed modes of vibration which are intended to represent approximate extremes of frequencies magnitude as far as Raman excitation is concerned, type II appearing more likely than type I.

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[13] Bernal and Tamm, *Nature*, **135**, 229 (1935).

[14] Gross and Vuks, *J. phys. radium*, **7**, 113 (1936).

[15] Pauling and Huggins, *Z. Krist.*, **A87**, 205 (1934).

I. The four-coördinated water molecule is vibrating about its equilibrium position against the remainder of the crystal, considered rigid and of infinite mass. In this case the effective force constant can be shown to be approximately twice that of the hydrogen bond, *k*. Thus

$$2k = 4\pi^2C^2\mu\nu^2 = 1.054\nu^2 \qquad (24)$$

where μ is the mass of the water molecule.

II. Two four-coördinated molecules are vibrating against each other along the direction of their common hydrogen bond, each being restrained also by its remaining three hydrogen bonds to the remainder of the crystal, considered rigid and of infinite mass. In this case, it can be shown that

$$3k = 4\pi^2c^2\mu\nu^2 = 1.054\nu^2 \qquad (25)$$

From eq. (21) and the criterion of equilibrium, $V'_{\text{O---O}}(d_0) = 0$, one obtains

$$b\gamma' e^{-bd_0} = 17.1 \qquad (26)$$

Hence, from eq. (19)

$$D_{\text{OHO}} = 8.47 - \gamma' e^{-bd_0} = 8.47 - 17.1/b \qquad (27)$$

and from eq. (23)

$$k_{\text{OO}} = -30.5 + b^2\gamma' e^{-bd_0} = -30.5 + 17.1\ b \qquad (28)$$

(k, the force constant of the hydrogen bond, in the usual units of dynes per cm., is equal to 0.69 k_{oo}).

The O–O Morse function was estimated by various means with resulting b values ranging from 2.5 to 3.0. The extreme values give, respectively, the limits 125 and 165 cm.$^{-1}$ for the frequency of vibration of the water molecule against the remainder of the crystal, type I, and the limits 155 and 200 cm.$^{-1}$ for the mutual vibration of two water molecules, type II. The corresponding dissociation energies of the hydrogen bond are 1.6 kcal. per mole for $b = 2.5$ and 2.8 kcal. per mole for $b = 3.0$. While all these values are of the proper order of magnitude to leave little doubt as to the correctness of the present interpretations of the nature of the low frequency Raman scattering of ice and water, they are definitely low, suggesting that a better representation of the oxygen–oxygen repulsion might be obtained by the use of larger b values.

4. The Energy of Dissociation of the Hydrogen Bond.—By using the experimental data to fit both the linear and quadratic term of the potential function $V_{\text{O---O}}$ a somewhat better approximation to the energy of dissociation of the hydrogen bond should be obtained. The values of b corresponding to vibrations of types I and II are 3.75 and 3.1, respectively. The corresponding limits of the dissociation energy of the hydrogen bond are 3.9 and 3.0 kcal. per mole. Since Raman excitation of the type II motion appears more plausible we favor the latter value. These values are in the range one expects from the comparison of the heat of sublimation of ice with those of the similar solids SO_2 and H_2S. Assuming intermolecular bond formation in the latter two to be negligible compared to that in H_2O, one finds that about half the energy of sublimation of ice is probably due to interactions other than those of hydrogen bond formation, giving approximately 3 kcal. per mole per hydrogen bond broken. Of course, in our calculation the hydrogen bond has been so represented as to imply that it was the only factor responsible for interaction of the molecules, and we should accordingly compare the calculated value of about 3 kcal. per mole per bond to the observed value of 5.9 kcal. per mole per bond. On the other hand, liquids in which the hydrogen bond is absent show very small perturbations of the intramolecular frequencies in the liquid state. Hence it may be significant that the calculated value, based primarily on the perturbation of the molecular vibrations by hydrogen bond formation, comes out with the proper order of magnitude to represent the energy of the hydrogen bond exclusive of the factors which contribute to intermolecular energy in systems where bond formation is of minor importance.

5. Perturbation of ν_δ by Hydrogen Bond Formation.—For the purpose of studying the perturbations of the symmetrical bending frequency, ν_δ, of the water molecule, a sufficiently accurate dynamical model is obtained by considering a harmonic oscillator with a force constant

$$2k/r^2 = 4\pi^2c^2\mu\nu\delta^2 \qquad (29)$$

where $(^1/_2)k(\Delta\phi)^2$ gives the potential energy as a function of the valence angle, ϕ, and μ is the mass of a hydrogen atom. Using again the observed frequency in preference to the extrapolated frequency at infinitesimal amplitude, and ignoring the deviation of water angle from the tetrahedral angle, one obtains

$$2k/r^2 = 0.0585(1595)^2 = 1.49\cdot 10^5 \qquad (30)$$

As in the case of hindered rotation, we can most conveniently calculate the perturbation of the P$''$ type of coördinated molecule, in which case the above restoring force is reduced by the ratio $(0.97/0.99)^2$ because of the stretching of the chemical O–H bond by the formation of the hydrogen bond H---O, and augmented by the amount 1.56 $V'_{\mathrm{H---O}}(r_0')/r'_0 = 0.186 \times 10^5$ (eq. 16), giving

$$4\pi^2c^2\mu(\nu''_\delta)^2 = 1.62 \times 10^5,\ \nu''_\delta = 1665 \text{ cm.}^{-1} \quad (31)$$

This value of ν''_δ, which is shifted toward higher frequencies from ν_δ by 70 cm.$^{-1}$, is in agreement with the maximum of the observed Raman band of water at 1656 cm.$^{-1}$, thus falling at about the same relative position in this band as did the ν''_{R} and ν''_π components in their respective bands. Hibben's curve for ice shows the maximum of this band to be shifted to still higher frequencies due to the presence of relatively more four-coördinated molecules. The calculation of the perturbed ν''_δ at a *higher* frequency than the unperturbed ν_δ is a striking confirmation of the essential correctness of the entire treatment.

6. **Combination Frequencies.**—The only feature of the Raman spectrum of water below 3700 cm.$^{-1}$ which remains to be accounted for is the band with a maximum at 2170 cm.$^{-1}$. This has usually been designated as a combination of ν_δ and ν_{R} the frequency of hindered rotation, a designation with which we agree. In fact, there is no other obvious way to account for this band. It is much wider than the ν_δ band, indicating the plausibility of the very wide ν_{R} being involved in its assignment. The frequency of maximum intensity is considerably less than the sum of the maxima of ν_δ and ν_{R} (1656 + 610 = 2266), but this is exactly what one might expect from the combination of two frequencies having such large amplitudes, especially in view of the very low maximum in the potential energy function which "hinders" the rotation of the water molecule. The harmonic approximation to the potential energy is naturally poor under these conditions and the interaction terms may well be very large. This same factor no doubt contributes to the unusual intensity of this band, considered as a combination frequency, for the usual treatment which predicts low intensity for combination and overtone frequencies is strictly applicable to only harmonic or nearly harmonic oscillations.[16]

Various bands have been reported at frequencies greater than 3700 cm.$^{-1}$. Some of the confusion which exists in the location of these high frequencies is probably due to the same factors we cited to account for the apparent disagreements at lower frequencies. Bands of frequency higher than the main band should be overtones or combinations of the frequencies we have already described.

V. Concluding Remarks

The calculations using modified Morse functions are subjected to many approximations which required the resulting deductions to appear in classical rather than quantum mechanical form.[17] Attention might be called to the fact that the oxygens are oscillating over relatively large amplitude. Even for $n_{\mathrm{O}} = 0$[17] the classical amplitude of the O–O oscillation would permit the oxygen–oxygen separation to vary over a range of more than ±0.1 Å. from the mean value of 2.76 Å. This is undoubtedly important to remember when interpreting X-ray diffraction curves such as those of Katzoff.[4] The maximum of the density distribution curve for liquid water at 2.9 Å. is interpreted by the authors to represent the scattering due to oscillating hydrogen-bonded water molecules plus that due to the "contacting" non-bonded water molecules. Even if close-packed water molecules were separated by more than 3 Å., X-ray measurements would still be unable to resolve their contribution from that of the coördinated structures. Thus Katzoff's maximum at 2.9 Å. may indicate that the close-packed structure in liquid water has a mean water molecule separation of over 3 Å., or at least considerably greater than the mean separation of the hydrogen-bonded oxygens. A similar explanation holds for the second maximum of Katzoff's density–distribution curve. The near-doubling at 3.9–4.5 A. in the distribution at 3° may possibly be due to the fact that molecules oscillating through large amplitudes (with high quantum numbers) tend to spend most of their time near the extremums. (Vibrations which most affect the separations of non-bonded or non-contacting water molecules would have very low frequency and hence appear with high quantum

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(16) Our calculations of the hindered rotation frequency are also subject to this same poor approximation, but the order of magnitude is, of course, unaffected.

(17) To call attention to one of these in particular, consider the variation of the frequency of the components in the main band with temperature. A better approximation than the one we used would be obtained by considering the O—H---O linear oscillator which would have two internal degrees of freedom with energy levels specified by two quantum numbers, n_{H} and n_{O} corresponding roughly to the modes of vibration $\cdot\leftarrow\quad\cdot$ and $\leftarrow\quad\leftarrow\qquad\rightarrow$, respectively. Our treatment attempted to determine the effect upon the observed transition $n_{\mathrm{H}} = 0 \longrightarrow 1$ of allowing n_{O} to have different distributions through $n_0 = 0, 1, 2, \ldots$ etc. Thus each of the many components we give for the main band of water is split into sub-components depending upon n_0 and the classical calculation of the shift of the maximum with temperature must necessarily be only a rough approximation.

numbers, even at 0°.) Katzoff's results, as well as ours, indicate that relatively small changes in the structure of water take place in the range 0–100°.

Estimates of the number of hydrogen bonds broken by fusion cannot very well be made from the latent heat of fusion. Holding the water molecules in a tetrahedral lattice necessarily involves some strain energy since the hydrogens in free water molecules tend to orient at less than the tetrahedral angle. This strain energy may be estimated as not over 300 cal. per mole. However, the breaking of only a small percentage of the hydrogen bonds appears to cause a collapse of the tridymite structure, and may relieve practically all the strain. This would cancel much of the energy effects of dissociating the first few bonds. Exclusive of the many other factors which influence energy of fusion, the effects of strain indicate that the coördination of water at 0° is less than that indicated by the heat of fusion. New experiments on ice and water just below and above 0° should yield interesting information concerning the role of the hydrogen bond in the fusion process.

An empirical treatment with Morse functions would appear from our results to be superior numerically to any straightforward theoretical treatment so far applicable to such complex systems. The approximate agreements which were obtained with experimental values in the empirical calculations presented here are interpreted by the authors as a tribute to the usefulness of the Morse function in representing interactions of atomic and molecular systems for which straightforward theoretical procedures are hopelessly cumbersome.

The general acceptance of the structure of water upon which this treatment of the Raman spectrum of water was based seems now to be assured. The success of our attempts to explain the complex experimental data here presented and analyzed can be taken not only as a new confirmation of prevailing ideas, but also as a satisfactory application of a new method of studying quantitatively the effects of hydrogen bond formation and association in liquids.

The authors wish to acknowledge their indebtedness to Professor Linus Pauling for helpful discussion of the material presented.

Summary

The Raman spectrum of liquid water over a wide range of temperatures, of ice at 0°, and of deuterium oxide were measured with high dispersion. Excitation was almost exclusively due to the 2537 Å. line of the mercury argon discharge lamp and the spectra are presented in the form of microphotometer records.

The results are discussed on the basis of the prevailing notion of a broken-down ice structure for liquid water. The perturbations of the radial vibration frequencies of the nine types of coordinated water molecules possible in such a structure are calculated from two experimentally determined constants: Δ, the perturbation of an OH oscillator due to hydrogen bonding through its hydrogen to another oxygen, and δ, the perturbation of the OH oscillator due to hydrogen bonding through its oxygen to the hydrogen of another oscillator. The resulting frequency patterns satisfactorily explain the structure and variations with temperature of the main band of ice and water.

Semi-quantitative estimates are made of the relative amounts of the different coördination types of water molecules. Water appears to average slightly more than two-coördinated in the range 25 to 90°, and is slightly less coördinated than is deuterium oxide. The two-coördinated structures predominate in both liquids. In ice at 0° the four-coördinated structure predominates but appreciable amounts of the three- and two-coördinated molecules were found to be present.

An empirical treatment of the perturbing potentials in terms of Morse functions gives the means of estimating the intermolecular frequencies. The results confirm already existing identifications for the "hindered translation" and "hindered rotation" frequencies. It is not necessary to postulate a combination of the two to account for all the data. The "hindered translation" was measured in ice as a sharp band with maximum at 210 cm.$^{-1}$. The bending frequency of water is shown to be shifted toward higher frequencies by the perturbations of the coördinated structures, in agreement with the observed Raman band.

The assignment of the band with maximum at 2170 cm.$^{-1}$ as a combination of the bending frequency with the hindered rotation frequency is discussed and accepted.

This analysis covers all the major features of the liquid water Raman spectrum and is confirmed both qualitatively and quantitatively by the

Raman spectrum of liquid heavy water and of ice.

The empirical treatment of the perturbing potentials as modified Morse functions leads to an estimate of the energy of the hydrogen bond in water as about 3 kcal. per mole per bond.

The essential agreement of the results of this analysis with X-ray data on liquid water is discussed and the usefulness of Raman spectra as tools for further studies of associated liquids is suggested.

STANFORD UNIVERSITY, CALIF.

RECEIVED MARCH 26, 1937

NOTES

The Molecular Structures of the 2,3-Epoxybutanes: a Correction

BY L. O. BROCKWAY AND PAUL C. CROSS

In the recently published report of the electron diffraction investigation of the 2,3-epoxybutanes[1] it was incorrectly stated that the identification of the geometric isomers was the same as that found in the chemical[2] investigation. Because of this misapprehension the electron diffraction investigation has been repeated and extended, and the consideration of new molecular models has led to the assignment supported by the chemical investigation.

The original preparations were refractionated and samples were taken having the boiling point ranges, 52.9–53.7 and 59.3–59.9°, respectively, at 746 mm. For each substance the new electron diffraction photographs have a lighter background, the diffraction pattern is more distinct and measurements of the ring diameters are more reliable than on the earlier photographs. The same characteristic features appear as before, however; and although the photographs of the two substances again look very much alike, the chief distinguishing feature is still observed, *i. e.*, photographs of the low boiling modification show a well-defined shoulder on the inside of the second strong maximum near $s = 10$ (see Fig. 1, reference 1).

In the models previously considered it was assumed that the strain introduced in the bond angles on each of the central carbon atoms by the formation of the three-membered ring was distributed only among the angles involving the carbon–oxygen bond. Of the six angles between the four bonds the angle in the ring is 57°26′, the other two strained angles are 125°10′, and the three remaining angles have the value 109°28′. It seems probable that the strain is more widely distributed; and accordingly new curves have been calculated on the basis of models in which the strain of the small angle is divided among four other angles and also on models in which all five of the other angles divide the strain. These curves are very similar, and the pair corresponding to a small angle of 57°26′ and five equal angles of 117°20′ is reproduced in Fig. 1. It will be observed that the inner

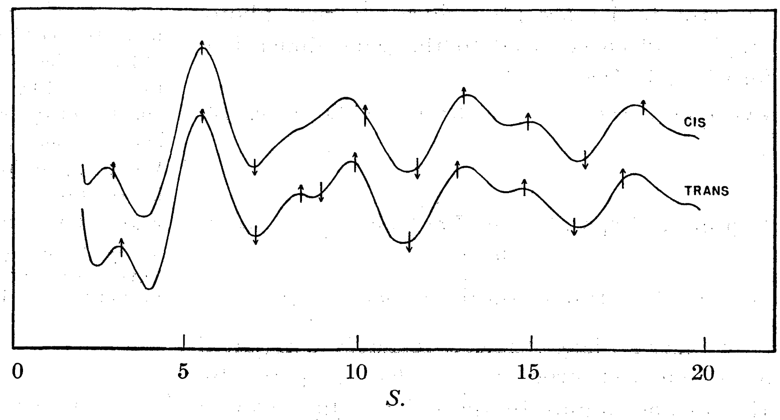

Fig. 1.—Theoretical electron scattering curves for models of the *cis* and *trans* 2,3-epoxybutanes in which five bond angles on each of the central carbon atoms divide equally the strain due to the formation of the three membered ring. The arrows represent maxima and minima observed on the photographs.

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[1] L. O. Brockway and Paul C. Cross, THIS JOURNAL, **58**, 2407 (1936).

[2] C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

shoulder on the second strong maximum now appears in the curve for the *trans* form, and accordingly the modification which boils at 53.5° (746 mm.) has the *trans* configuration. It may be mentioned that the new photographs from each of the compounds show the inner maximum (near $s = 3$) with that for the *trans* form having a slightly greater s value in agreement with the curves. That this identification is not based on more extensive data is due to the fact that the two expressions for electron scattering by the *cis* and *trans* forms show only slight differences. In the chemical investigation[2] the *trans* form was identified as that one which was obtained in an optically active state and this choice is now supported by the electron diffraction result. The *cis* form is that boiling at 59.6° (746 mm.).

Accepting the chemical identification of the isomers, we see that the electron diffraction study offers proof that bending the carbon–oxygen bond in forming the three-membered ring also bends the other bonds from their "natural" or unstrained positions, since the model in which the bending effect is confined to the one bond leads to the wrong identification of the isomers.

The interatomic distances previously reported are still to be accepted since the new photographs and curves lead to the same dimensions for the molecules.

PASADENA, CALIF.
RECEIVED MARCH 29, 1937

Improved Preparation of Pentaacetyl-keto-fructose

BY FRANCIS B. CRAMER AND EUGENE PACSU

Pentaacetyl-keto-fructose, formerly designated as α-pentaacetylfructose, was first prepared by Hudson and Brauns[1] by the action of zinc chloride and acetic anhydride on fructose. The yield was less than 8% of the theoretical. Acetylation of fructose with acetic anhydride and pyridine gave rise to the same compound in less than 5% yield. When tetraacetylfructose is prepared by the improved method of Pacsu and Rich,[2] and this converted into the keto-pentaacetate by the procedure of Hudson and Brauns,[1] the yield, calculated on fructose, is increased to 36%. A procedure has now been worked out by which the keto-pentaacetate may be obtained in about 50% yield by the direct acetylation of fructose without the isolation of an intermediate compound. The production of a good yield of pentaacetyl-keto-fructose appears to take place under conditions which facilitate the preliminary formation of a large amount of β-tetraacetylfructose. As amply demonstrated by Hudson and Brauns,[1] the keto-pentaacetate, once formed, is unaffected when heated with zinc chloride and acetic anhydride in the concentrations used in our experiments.

Experimental

Preparation of Pentaacetyl-keto-fructose.—Ten grams of finely powdered fructose was added in one portion to a solution of 1 g. of fused zinc chloride in 100 cc. of distilled acetic anhydride cooled in an ice-bath. The mixture was stirred vigorously at 0° for four hours, during which time most of the sugar dissolved. The temperature was then kept at 20–25° for one hour and finally at 50° for two hours. The cooled solution was stirred with an equal volume of water for one and one-half hours, further diluted, and neutralized with an excess of sodium bicarbonate. The chloroform solution of the gummy precipitate was united with the chloroform extracts of the water solution, then dried with calcium chloride, filtered, and evaporated to a sirup *in vacuo*. The sirup was dissolved in about 50 cc. of absolute ether, and the solution on standing overnight in the ice-box deposited 10.3 g. of crystalline pentaacetyl-keto-fructose, having $[\alpha]^{20}_{\mathrm{D}}$ 33.5° in chloroform solution.

When half the above amount of acetic anhydride was used, the yield of the crystalline pentaacetate was 9 g. (42%). The keto-acetate was prepared more rapidly by stirring 10 g. of fructose with 50 cc. of acetic anhydride, and 1 g. of zinc chloride for one hour at room temperature and one hour at 50°. The yield was 7.5 g., or 35%. When 10 g. of fructose was stirred with the same acetylating solution at 50° for one hour and the reaction mixture worked up immediately, the yield was only 6 g., or 28%.

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RECEIVED APRIL 3, 1937

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[1] Hudson and Brauns, THIS JOURNAL, **37**, 2736 (1915).

[2] Pacsu and Rich, *ibid.*, **55**, 3018 (1933).

Physical Constants of Morpholine

BY V. H. DERMER AND O. C. DERMER

In preparing to study morpholine as an ionizing solvent, we have investigated its purification and measured some of its physical constants. Since the first shipment of morpholine we obtained apparently contained esters, we resorted to chemical purification through the acid oxalate. Later lots proved to be of extraordinary purity, requiring only to be dried over metallic sodium.

Table I gives the results of our measurements and calculations.

TABLE I

Constant		Value	Earlier values
Boiling point (760 mm.), °C.		128.9	128–130,[a] 128.3[b]
Freezing point, °C.		-4.9 ± 0.1	
Density, g./cc.		0.9994 20/4° vac.	1.0008 20/4°,[a] 1.0016 20/20°[b]
Refractive index, $n^{20}\text{D}$		1.4545	1.4540[a]
Molecular refraction	observed	23.60	23.54[a]
	calcd.[c]	23.72	
Viscosity, poises at 20°		0.0223	
Surface tension at 20°, dynes/cm.		37.5	
Parachor	observed	215.7	
	calcd.[d]	213.3	

[a] Knorr, *Ann.*, **301**, 1–10 (1898). [b] Wilson, *Ind. Eng. Chem.*, **27**, 870 (1935). [c] Atomic refractions from Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911); **79**, 134 (1912). [d] Atomic parachors from Bayliss, THIS JOURNAL, **59**, 444 (1937); Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).

Experimental

Commercial morpholine, purchased from Carbide and Carbon Chemicals Corporation, was added gradually to slightly more than a molar equivalent of oxalic acid dissolved in alcohol. The precipitated morpholine hydrogen oxalate was filtered out and recrystallized twice from 60% ethanol. Even then it did not melt sharply, but sintered and decomposed with effervescence at 190–195°. Titration with standard alkali gave indistinct end-points because of the morpholine liberated by hydrolysis; hence the oxalate was titrated with 0.1 *N* potassium permanganate. Molecular weight found: 178, 178; calcd. for $C_4H_8ONH(COOH)_2$, 177. Morpholine hydrogen tartrate was prepared similarly; it melts at 165–166°.

Morpholine was regenerated from the oxalate by adding the salt to concentrated aqueous potassium hydroxide. The layer of free base was separated and dried over solid potassium hydroxide and then sodium. It was then fractionally distilled from sodium through a three-ball Snyder column. After the first quarter had been set aside for further drying, the remainder had a corrected boiling point of 128.9°. This temperature was read on two thermometers, each newly calibrated with pure chlorobenzene and ethylene dibromide to avoid stem correction. Later distillations showed that it is unnecessary to subject good commercial morpholine to the oxalate method of purification; refluxing over sodium followed by fractionation gave a product of boiling point identical with that of the "purified" material.

The freezing point of freshly distilled morpholine was measured with several thermometers calibrated at 0° with pure ice. The refractive index at 20.0° was determined with a Zeiss dipping refractometer in a closed cell. At the same temperature, the surface tension relative to water was measured with Traube's stalagmometer, and the relative viscosity with an Ostwald viscometer. In all cases precautions were taken to exclude moisture and carbon dioxide from samples tested.

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RECEIVED APRIL 5, 1937

The Heat of Combustion and Structure of Cuprene

BY P. J. FLORY

In a recent study of cuprene formed by alpha ray polymerization of acetylene, Lind and Schiflett[1] have reported 265.3 kcal. for the heat of combustion per structural unit —(C_2H_2)—. Although the structure of cuprene has never been determined, they have calculated the heat of polymerization assuming the formation of one C=C and one C—C bond in place of each C≡C bond of acetylene and using Fajans'[2] heats of atomic linkages. The significance of the comparison of this calculated heat of polymerization with that deduced from the heats of combustion of acetylene and of cuprene was obscured by the approximate nature of Fajans' values.

A much more reliable heat of polymerization can be calculated from recent thermochemical data. In conformity with Lind and Schiflett's assumption regarding the constitution of cuprene, a chain structure in which the single and double bonds occur alternately, *i. e.*, $-(CH{=}CH)_n-$, will be assumed.

Expressing heats of combustion (Q) as heat

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[1] S. C. Lind and C. H. Schiflett, THIS JOURNAL, **59**, 411 (1937).

[2] K. Fajans, *Ber.*, **53**, 643 (1920).

evolved and heats of reaction (ΔH) as heat *absorbed* by the system

$$Q_u = 2Q_{CH_2} - Q_{H_2} - \Delta H_{hyd.}$$

where $\Delta H_{hyd.}$ is the heat of hydrogenation of the polymer per structural unit —(CH=CH) —, and Q_u, Q_{CH_2} and Q_{H_2} are the respective heats of combustion of the polymer per structural unit, of the hydrogenated polymer per $—CH_2—$ group, and of hydrogen. If the hydrogenation of the polymer is imagined to proceed by the hydrogenation of consecutive structural units, the hydrogenation of one unit is seen to be analogous to the partial hydrogenation of 1,3-butadiene to *n*-butene-1, for which $\Delta H_{hyd.} = -26.72$ kcal. per mole.[3] However, allowance should be made for the presence of the saturated substituent (previously hydrogenated) on the one carbon atom of the structural unit undergoing hydrogenation. Although heats of hydrogenation of compounds of the type $CH_2=CH—CH=CH—R$ have not been determined, Kistiakowsky and co-workers[4] have shown that monoalkyl substitution of an α-mono-olefin reduces the magnitude of $\Delta H_{hyd.}$ by about 2 kcal. Hence, the best value for $\Delta H_{hyd.}$ is approximately -25 kcal. Rossini,[5] from heats of combustion of gaseous hydrocarbons, has shown that $Q_{CH_2} = 157.0$ kcal. Taking $Q_{H_2} = 68.3$ kcal.,[5] one obtains for the combustion of the gaseous polymer $Q_u = 271$ kcal. Assuming about 4 kcal. for the heat of sublimation per structural unit, the heat of combustion of solid polymer becomes 267 kcal. per structural unit. This excellent agreement with Lind and Schiflett's experimental value for the heat of combustion of cuprene substantiates the structure assumed above.

Using 311 kcal. for the heat of combustion of acetylene,[6] Lind and Schiflett's experimental heat of combustion of solid cuprene leads to -46 kcal. for ΔH_p, the heat of polymerization of acetylene to cuprene; the calculated heat of combustion of solid cuprene leads to $\Delta H_p = -44$ kcal.; for the formation of gaseous cuprene ΔH_p (calcd.) = -40 kcal. In comparison, ΔH_p for the formation of gaseous linear polymers from gaseous ethylene or higher olefins is -23 kcal.[7]

WILMINGTON, DELAWARE RECEIVED MARCH 29, 1937

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[3] Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 146 (1936).

[4] *Ibid.*, **57**, 876 (1935); *ibid.*, **58**, 137 (1936).

[5] F. D. Rossini, *Bur. Standards J. Research*, **13**, 21 (1934).

[6] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

[7] Flory, THIS JOURNAL, **59**, 241 (1937).

Reduction of Nitroguanidine. VIII
The Formation of Aminoguanidine by Reduction in Liquid Ammonia Solution[1]

BY LAURENCE P. FULLER, EUGENE LIEBER AND G. B. L. SMITH

The study of the reduction of nitroguanidine in liquid ammonia solution with active metals is unrecorded. This note presents the results of the preliminary study of the behavior of nitro- and nitrosoguanidine in that medium, and describes the conditions necessary for the formation of aminoguanidine by their reduction with metallic sodium.

In contrast to their very low solubility in water and the usual organic solvents, nitro- and nitrosoguanidine were found to be very soluble in liquid ammonia, the latter forming a bright yellow solution. Either can be recovered unchanged by evaporation of the solvent. Addition of either nitro- or nitrosoguanidine to a solution of sodium amide in liquid ammonia causes no visible precipitation of a sodium derivative, and after the evaporation of the solvent the nitro- and nitrosoguanidine can be recovered unchanged. The addition of metallic sodium to a liquid ammonia solution of nitroguanidine produces an extremely vigorous reaction, the sodium undergoing very rapid dissolution. As sodium was added in successive portions to colorless solutions of nitroguanidine in liquid ammonia, a series of color changes and precipitations was obtained which paralleled exactly the reduction of nitrobenzene in liquid ammonia with sodium, as observed by White and Knight.[2] The solutions became yellow, then orange, reddish-orange and finally a murky brownish-orange, while a precipitate which at first is white, gradually darkens as the reduction proceeds. The return of the sodium blue color was taken as the end-point of the reduction.

The formation of nitrosoguanidine from nitroguanidine theoretically requires two atoms of sodium and when this amount of sodium was employed a yellow solution was produced. However, no nitrosoguanidine was obtained. On further addition of sodium, the blue color was always obtained before the six atoms of sodium, theoretically required for the formation of aminoguanidine, could be added. The molar ratios of

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[1] For more full details see M. S. Thesis by Laurence P. Fuller, Polytechnic Institute of Brooklyn, 1937. Contribution No. 33 from the Department of Chemistry of the Polytechnic Institute of Brooklyn.

[2] White and Knight, THIS JOURNAL, **45**, 1780 (1923).

sodium to nitroguanidine which were obtained to the blue color end-point varied from 3.7:1 to 4.5:1[3] depending on the quantity of the nitroguanidine taken. The residues obtained on evaporation of the ammonia contained no aminoguanidine. Cyanamide was definitely identified to the extent of 10%. Found, %Ag, 83.15; calculated for CN_2Ag_2, %Ag, 84.36. By treatment of the silver derivative with hydrogen sulfide, hygroscopic crystals of melting point 39.5°[4] were obtained.

During the reductions a vigorous evolution of gas takes place. Examination of the gas showed it to be pure nitrogen, and quantitative experiments showed that it was formed to the extent of 27 to 30% of the nitroguanidine taken. This corresponds to a molar ratio of nitrogen to nitroguanidine of 1:1. This suggests,[1] although we are unable to offer complete experimental proof at present, that nitroguanidine (a mixed anammonide of aquo nitric acid and an ammonocarbonic acid) is in some way subject to dearrangement[5] during the reaction (since nitroguanidine had been recovered unchanged from its solution in liquid ammonia or from a liquid ammonia solution of sodium amide) to form another ammono carbonic acid, cyanamide, and a mixed aquo ammono nitric acid, such as $NH_2{\cdot}NO_2$ (nitro-amide) which may be reduced to a mixed aquo ammono nitrous acid. This latter group is known to be unstable, giving N_2.[6] An examination of nitroamide in liquid ammonia with active metals is contemplated. Attempts to prepare aminoguanidine by reduction of a liquid ammonia solution of nitrosoguanidine with metallic sodium gave the same results as with nitroguanidine; no aminoguanidine was obtained.

It was found, however, that the nature of the reduction was changed profoundly if it was carried out in the presence of a solution of ammonium chloride in liquid ammonia. Here no color changes were observed, the solution of nitroguanidine and ammonium chloride remained colorless and only sodium chloride precipitated. Aminoguanidine was obtained only when the molar ratio of nitroguanidine to ammonium chloride was maintained at 1:6. At concentrations of ammonium chloride below this ratio, brilliantly red to reddish-brown substances, containing only small amounts of aminoguanidine, were obtained. Figure 1 summarizes the chief results obtained. It will be observed that by maintaining the molar ratio of nitroguanidine to ammonium chloride constant at 1:6, the hydrazino-(aminoguanidine) formation, as determined by the procedure of Jamieson,[7] is proportional to the molar quantity of sodium added. Substitution of ammonium acetate for ammonium chloride is without effect on the yield (Curve III, Fig. 1); however, doubling the concentration of ammonium chloride considerably lowers the formation of aminoguanidine (Curve II, Fig. 1). The aminoguanidine was identified by its conversion to benzalaminoguanidine, $C_6H_5CH{=}NNHC(NH)NH_2$; m. p. found, 178.5°; reported178.[8]

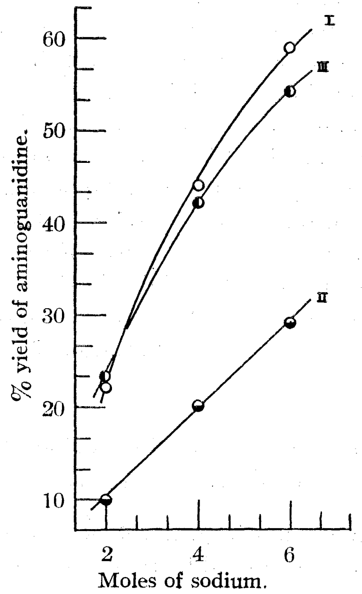

Fig. 1.—I, ○, nitroguanidine : ammonium chloride, 1:6; II, ◒, nitroguanidine : ammonium chloride, 1:12; III, ◐, nitroguanidine : ammonium acetate, 1:6.

Anal., Calcd. for $C_8H_{10}N_4$: N_2H_4, 19.75. Found: N_2H_4, 19.69. The yields of aminoguanidine for the ratio, sodium : nitroguanidine: ammonium chloride, 6 : 1 : 6, varied from 50 to 60%. By adding a mixture of sodium and ammonium chloride in the ratio of 1 : 1 to a solution of

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[3] Audrieth and Schmidt, University of Illinois, private communication, found substantially the same for nitroguanidine and sodium in liquid ammonia.

[4] Several values for the melting point of cyanamide can be found in the literature; 40° appears to be the average value given.

[5] Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, **61**, 437 (1926).

[6] Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Co., N. Y., 1935, p. 288.

[7] Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, N. Y., 1926, p. 36.

[8] Thiele, *Ann.*, **270**, 35 (1892).

nitroguanidine in liquid ammonia, yields of 60 to 70% were obtained.

While the ammonium salts of strong acids have been used for decomposition of sodium–liquid ammonia reduction products,[2] this work appears to be the first example in which an acidic solution of liquid ammonia was used to change the environmental condition of the liquid ammonia solvent media during reduction. The importance of the environmental conditions of the solvent media for the reduction of nitroguanidine has been demonstrated.[9] The mechanism will become clear when it is remembered that the ammonium ion is an ammoniated hydrogen ion

$$Na^\circ \longrightarrow Na^+ + e^-$$
$$H^+ + e^- \longrightarrow H^\circ$$

if, however, an oxidant be present

$$\text{Oxidant} + H^+ + e^- \longrightarrow \text{Reductant} + H_2O$$

It, therefore, appears probable that liquid ammonia could also serve as a solvent medium for catalytic hydrogenations in which molecular hydrogen is introduced into a liquid ammonia solution of an oxidant in the presence of a catalytically active metal. We are at present engaged in determining the usefulness of liquid ammonia as a solvent medium for catalytic hydrogenations, and in extending the mechanism of the reduction and behavior of nitroguanidine in that solvent.

[9] Lieber and Smith, THIS JOURNAL, **58**, 2170 (1936).

BROOKLYN, NEW YORK RECEIVED MARCH 26, 1937

Micro Analysis for Exchangeable Hydrogen

BY WILLIAM H. HAMILL

A technique has been developed for the determination of exchangeable hydrogen with 2–5 mg. of substance (water soluble, non-volatile) and 50–100 mg. of heavy water (98%) which is correct within 3%. The determination depends upon the decrease in density of the heavy water, due to exchange, as measured by a small quartz float[1,2] controlled by temperature at constant pressure. The density of the float was determined with potassium chloride solution, part of which was used for a pycnometric density determination at the same temperature as that required for flotation equilibrium.

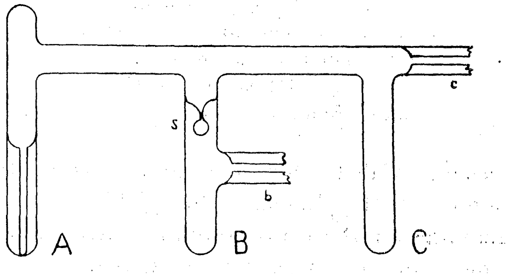

Fig. 1.—Exchange vessel.

Exchange analyses were made in a Pyrex vessel, hereafter referred to as the still (Fig. 1). The float was introduced into the capillary A, the substance into B and the heavy water, in a sealed ampoule, into C. The still was evacuated to about one micron through b and c and sealed. The heavy water was released by immersing C in dry ice, the freezing water shattering the ampoule, and distilled into A for a density measurement. The water was then distilled into the bulb-seal which was broken by freezing in dry ice.[3] The substance was dissolved and the water distilled off quickly at room temperature by cooling C with dry ice. The water was then distilled into A and the density redetermined. This process was repeated to ensure complete solution and exchange.

The number of exchangeable hydrogen atoms per molecule of substance was calculated from equation (1) with a parallel experiment upon a reference substance to minimize errors arising from exchange with glass, temperature coefficient of density of heavy water, etc. Three determinations with urea served for reference.

$$n_1/n_2 = W_1M_1\Delta t_1S_2N_2/W_2M_2\Delta t_2S_1N_1 \qquad (1)$$

n = number of exchangeable hydrogen atoms per molecule
S = weight of substance
M = molecular weight of substance
N = mole fraction D_2O after exchange
W = weight of heavy water
Δt = difference in flotation temperatures due to exchange

The results of these analyses appear in Table I and refer to immediate exchange (three minutes) at room temperature except as noted. Ogawa's[4] observation of slow exchange for urea (60% in five minutes) was not confirmed. Hydrogen in the methylene group of malonic acid has been shown

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[1] The float, about 8 mm. × 0.6 mm., is maintained upright by means of a quartz bead at one end. The float accelerates 0.01 cm. sec./1° at 30–35°. The effect of pressure upon the density of the float, with respect to heavy water, is only $1(10)^{-5}/1$ atm.

[2] A Pyrex micro float has been employed by Goldfinger and Scheepers, *Compt. rend.*, **198**, 1916 (1934).

[3] This seal is easy to make and positive in action, not failing once. The water freezes quickly at the constriction, sealing the bulb which is broken within two minutes.

[4] Ogawa, *Bull. Chem. Soc. Japan*, **11**, 367 (1936).

to exchange[5] completely in five hours at 100°. In the present work the first two (carboxyl) hydrogen atoms were found to exchange at once, the other two more slowly with a half time of fifteen minutes. The sixth hydrogen atom in histidine hydrochloride apparently is due to a rapidly established equilibrium which corresponds

$$-\mathrm{NH}-\mathrm{CH}{=}\mathrm{N}- \;=\; -\mathrm{N}{=}\mathrm{CH}-\mathrm{NH}-$$

to known methyl derivatives. The fifth slowly exchanging hydrogen atom in vitamin B_1 hydrochloride is not accounted for but agrees with an observed[6] second titratable equivalent of acid in the vitamin with a slow approach to equilibrium. The rate of this slow exchange was measured with 3.2 mg. of vitamin and 76 mg. of heavy water at 37°. Initial, final and four intermediate observations gave a first order velocity constant (min.$^{-1}$ log$_{10}$) $k = 4.3(10)^{-3}$.

This method is more tedious than the one recently described by Williams[7] but has the principal advantage of distinguishing between active hydrogen, as in hydroxyl and amino groups, and labile, slowly exchanging hydrogen, as in the methylene group of malonic acid. Also, since evacuation of the still precedes exchange there is no difficulty with hygroscopic substances. The sensitivity is high, 10^{-5} equivalent of substance in 50 mg. of heavy water lowering the flotation temperature by 0.3° at 30°.

TABLE I

Substance	n
Urea	(4.00)
Glycine	3.13
Histidine, HCl	6.07, 6.36
Vitamin B_1HCl natural	3.94^{a,b} 4.83
Vitamin B_1HCl synthetic	3.6^{a,c} 4.5
Hydroquinone	1.95
Sodium formate	0.00
Succinic acid	2.14, 2.06
Malonic acid	2.0^{a} 3.99

[a] The first value is due to immediate exchange, the second is a final value following an additional slow exchange. [b] The author is indebted to Dr. L. R. Cerecedo and Dr. D. J. Hennessy for the natural vitamin which was extracted from rice polishings. [c] The difference in values between natural and synthetic vitamin may be due to mechanical loss during evacuation in this experiment.

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RECEIVED MARCH 29, 1937

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(5) Wynne-Jones, *Chem. Rev.*, **17**, 115 (1935).

(6) Williams and Ruehle, THIS JOURNAL, **57**, 1856 (1935).

(7) Williams, *ibid.*, **58**, 1819 (1936).

A Rapid Method for the Determination of Lactoflavin in Milk[1]

BY C. H. WHITNAH, BERNICE L. KUNERTH AND M. M. KRAMER

The determination of lactoflavin (vitamin G) by new fluorimetric methods[2] is complicated by elaborate preparation recommended for the sample.[3] It had been observed in this Laboratory that the trichloroacetic acid serum from milk used for vitamin C titrations[4] often had a greenish color whereas the mercuric nitrate serum used for the determination of sugar was colorless. This suggested that fluorimetric tests for flavin might be applied to the former serum.

The following procedure has been used. Add 15 ml. of 10% trichloroacetic acid to 10 ml. of milk, let stand thirty to sixty minutes, centrifuge five minutes at about 2000 r. c. f. Neutralize[5] 10 ml. of the resulting serum, with methyl orange as indicator, and dilute until the sample can be matched in the light of an Eveready Fluoray lamp,[2] with standard flavin solutions (Labco PX grade) containing 0.12 to 0.06 gamma of flavin per ml. Calculate flavin content on the basis of dilutions made. Dilutions until the portions read contain less than 0.12 gamma per ml. seem essential as the values for stronger solutions are easily underestimated.

It was repeatedly shown that a sample of milk tested the same on successive days. Differences between milk samples from different cows were also found to be consistent.

The method was checked by recovery experiments. Duplicate samples of milk were reinforced with lactoflavin (measured amounts of the standard solution) to contain approximately 2 and 3 times the original lactoflavin content. Values secured by calculation and by determination with the Fluoray lamp compared as follows.

	Lactoflavin per ml.		Diff. from calcd. value per ml.	
	Calcd.	Determined by lamp		
	γ	γ	γ	%
(1) Milk	..	1.34	..	..
(2) 9 ml. milk + 11.44 γ flavin made up to 10 ml.	2.35	2.12	0.23	10
(3) 9 ml. milk + 22.87 γ flavin made up to 10 ml.	3.49	3.19	0.30	9

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(1) Contribution No. 233, Department of Chemistry and No. 67, Department of Home Economics.

(2) Supplee, Ansbacher and Bender, *J. Biol. Chem.*, **110**, 365 (1935).

(3) Kuhn, György and Wagner-Jauregg, *Ber.*, **66**, 1034 (1933).

(4) Whitnah and Riddell, *J. Dairy Sci.*, **20**, 9 (1937).

(5) Kuhn and Moruzzi, *Ber.*, **65**, 888 (1932).

Recoveries were only 10% less than the calculated values.

Other composite milk samples have been used for biological assay by the Bourquin-Sherman[6] method, shown[7] to measure the flavin factor. The rats, kept for the customary eight-week period, produced satisfactory composite growth curves. Estimates of the lactoflavin or vitamin G content of the samples were made from the composite growth curves of the rats, compared with the reference curve of rats fed the standard lactoflavin, shown in the table.

Five biological estimates checked the rapid chemical determinations with a maximum difference of 25% as indicated.

Supplements Milk	No. rats	Daily portion, ml.	Av. gain for 8 weeks, g.	Estimated flavin per ml. milk, γ	Flavin per ml. milk Fluoray lamp, γ	Diff. from biological value per ml. γ	%
A	10	3	43	2.2	2.30	+0.10	+ 4
B	10	3	40	2.0	1.76	− .24	−12
C	10	3	46	2.3	2.20	− .10	− 5
D	10	3	54	2.6	2.55	− .05	− 2
E	10	3	50	2.5	1.88	− .62	−25
Lactoflavin		γ		Animals for reference curve			
	9	5.0	33				
None	25	..	±0	Negative control animals			

Effort is being made to apply this rapid method to colostrum, shown by biological work in our laboratory to be higher in lactoflavin content than ordinary milk. Certain characteristics of the colostrum, due to physical or chemical properties, present difficulties not yet overcome.

KANSAS AGRICULTURAL EXPT. STA.
MANHATTAN, KANSAS

RECEIVED APRIL 20, 1937

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[6] Bourquin-Sherman, THIS JOURNAL, **53**, 3501 (1931).

[7] Booher, Blodgett and Page, *J. Biol. Chem.*, **107**, 599 (1934); Bisbey and Sherman, *ibid.*, **112**, 415 (1935).

COMMUNICATIONS TO THE EDITOR

THE THERMAL DECOMPOSITION OF α-TOCOPHEROL

Sir:

Last year, H. M. Evans, O. H. Emerson and G. A. Emerson [*J. Biol. Chem.*, **113**, 319 (1936)] reported the isolation from wheat germ oil and later from cottonseed oil [*Science*, **83**, 421 (1936)] of alcohols having the biological properties of vitamin E. These substances were named "tocopherols" and appear to be isomers with the empirical formula $C_{29}H_{57}O_2$, and to be chemically closely related. Structurally, it is known that the compounds contain a hydroxyl group which accounts for one of the oxygen atoms.

I have recently investigated α-tocopherol, the most active of these substances, using material prepared from cottonseed oil, and wish to report certain observations on the behavior of this compound at higher temperatures which seem to permit deductions to be drawn regarding the constitution of α-tocopherol.

When α-tocopherol is heated decomposition sets in at 350° and a crystalline sublimate is obtained as well as an oily distillate. The crystalline material is very readily obtained in the pure state and its investigation led to a formula $C_{10}H_{14}O_2$. A literature search revealed its close resemblance to durohydroquinone and the identity was established by direct comparison with a sample of this compound kindly furnished through the courtesy of Professor Lee Irvin Smith of the University of Minnesota. Both the diacetyl derivative and the quinone were also prepared and compared by mixed melting point determinations with the corresponding derivatives of the known durohydroquinone.

ANALYSES AND MELTING POINTS

Compound		Diphenol	Diacetate	Quinone
M. p., °C.		230	201	111
Formula		$C_{10}H_{14}O_2$	$C_{14}H_{18}O_4$	$C_{10}H_{12}O_2$
Calcd.	C, %	72.28	67.18	73.14
	H, %	8.40	7.25	7.36
Found	C, %	72.29 72.32	67.12	73.42
	H, %	8.54 8.46	7.21	7.41

The above findings seem to be best explained by assigning the structure of a mono-ether of durohydroquinone to α-tocopherol. The ultraviolet spectrum of α-tocopherol is very similar to that of hydroquinone as has been pointed out to me by Dr. Oliver H. Emerson. Its insolubility in alkalies and its high reducing power, as well as the lack of reducing properties in its esters are also in good agreement with such an assumption.

My present efforts are mainly directed to an elucidation of the alkyl portion of α-tocopherol. On completion of these investigations I intend to publish the details of the above experiments. I wish to express my appreciation of the assistance of Professor H. M. Evans and Dr. Oliver H. Emerson of the University of California who kindly advised me on the production of α-tocopherol and who assayed various concentrates during its preparation.

RESEARCH LABORATORIES E. FERNHOLZ
MERCK & COMPANY, INC.
RAHWAY, N. J.

RECEIVED MAY 20, 1937

CIS-TRANS ISOMERIZATION BY BROMINE ATOMS

Sir:

An investigation to ascertain whether halogens and halogen acids add "*cis*" or "*trans*" to maleinoid (*cis*) or fumaroid (*trans*) forms of unsaturated substances has been under way in this Laboratory for some time. It is evident that for a complete understanding of this problem it is necessary to know the effectiveness of the addition reagent causing the transformation of the "maleinoid" and the "fumaroid" form. Yet, while numerous observations on the rearrangement in solution of the "maleinoid" to the "fumaroid" form are available, no critical study has been made of the inter-relationship of the reagents responsible for the transformation, and no comprehensive hypothesis has been advanced which would correlate these diverse observations.

We have found that in the dark, in two hours, carefully purified isostilbene, dissolved in benzene, is not isomerized to stilbene by hydrogen bromide when the reactants are mixed either in air or in a highly evacuated tube, or in the presence of antioxidants (*e. g.*, hydroquinone, catechol, thiophenol). However, the addition of a peroxidic substance (*e. g.*, benzoyl peroxide, ascaridole) to the reaction mixture caused complete isomerization to stilbene in a few minutes. The time required for complete conversion varied with the amount of the peroxide used, but even minute traces of peroxides caused complete conversion in thirty minutes.

In direct sunlight or in artificial light, isostilbene, dissolved in benzene, is transformed to stilbene by hydrogen bromide in about five minutes. Here evacuation of the reaction vessel had a pronounced effect in that twenty minutes was required for complete isomerization. Most striking, however, is the effect of antioxidants. Thus, hydroquinone, ethyl mercaptan, etc., completely prevent the transformation of isostilbene to stilbene by hydrogen bromide in the light, either in the presence or absence of air.

Furthermore, no isomerization of isostilbene to stilbene was observed under any of the above conditions (antioxidant or peroxidic, in the light or in the dark) with hydrogen chloride. Neither has a mixture of bromine and hydrogen bromide caused isomerization in the dark. The halogens are well known to cause isomerization in the light.

The above experiments lead us to believe that bromine atoms[1] are the active catalysts in this transformation. They would be produced by the action of oxygen or a peroxide, or by light, on hydrogen bromide. Once produced, they convert isostilbene to stilbene by a chain reaction. The ineffectiveness of hydrogen chloride in causing isomerization is thus readily explainable on the basis of its relative stability toward oxygen.

Several investigators[2] have observed that alkali metals and traces of certain organo-alkali compounds cause similar isomerizations. We are, therefore, engaged in an extensive study to evaluate the part played by atoms in such conversions, and the role of other agencies.

[1] The hypothesis that bromine atoms are responsible for the "peroxide effect" in the addition of hydrogen bromide to unsaturated molecules is proposed in an article by M. S. Kharasch, H. Englemann and F. R. Mayo, in the *Journal of Organic Chemistry*, in press.

[2] Meerwein and Weber, *Ber.*, **58**, 1266 (1925); Schlenk and Bergmann, *Ann.*, **463**, 107–117 (1928); Ziegler and Wollschitt, *ibid.*, **479**, 129–131 (1930).

JONES CHEMICAL LABORATORY M. S. KHARASCH
UNIVERSITY OF CHICAGO J. V. MANSFIELD
CHICAGO, ILLINOIS F. R. MAYO

RECEIVED MAY 18, 1937

PHOTODECOMPOSITION OF CHLORINE DIOXIDE IN CARBON TETRACHLORIDE SOLUTION

Sir:

We have investigated recently the bromine sensitized photodecomposition of chlorine dioxide in carbon tetrachloride solution and find that appreciable amounts of Cl_2O_6 are formed during the reaction. A reinvestigation of the unsensitized decomposition of chlorine dioxide in carbon tetrachloride solution using λ = 3650 Å. showed that here also relatively large amounts of Cl_2O_6 are formed.

Chlorine dioxide solutions were insolated for some time and then forced into water and shaken. A heavy mist was observed similar to that which forms when Cl_2O_6 reacts with water. Chlorine dioxide and chlorine were removed from the water extract by aspirating air through it for three hours. The resulting solution was neutralized with potassium hydroxide and evaporated. Microscopic examination of the crystals obtained indicated potassium chlorate and potassium perchlorate. The presence of ClO_4^- was also demonstrated by characteristic crystals formed when a drop of 2% brucine solution was added to a drop of the test solution on a microscope slide. The outside of the spot was surrounded by a brown ring which is also characteristic of ClO_3^-. The tests were compared with similar tests on pure substances. The chloric acid and perchloric acid can be explained by the formation of Cl_2O_6 which reacts with water according to

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

Qualitative tests on the water extract also indicated small amounts of hypochlorous acid, presumably due to Cl_2O.

$$Cl_2O + H_2O \longrightarrow 2HClO$$

Methods for the quantitative estimation of chlorine dioxide, chlorine, hypochlorous acid, chloric acid and perchloric acid in the water extract have been developed and checked. The relative amounts of the different components depend in a rather complicated way upon such factors as concentrations, light intensity and time of insolation. This is to be expected since Cl_2O_6 and Cl_2O are themselves photosensitive.

The point which we wish to stress in this note is that relatively large amounts of Cl_2O_6 are formed (corresponding in some experiments to as much as 20% of the chlorine dioxide decomposed). This is in contradiction to the findings of previous workers [E. J. Bowen, *Trans. Faraday Soc.*, **27**, 513, (1931); Y. Nagai and C. F. Goodeve, *ibid.*, **27**, 508, (1931)], who report only chlorine and oxygen. The formation of Cl_2O_6 indicates that the above reactions in solution probably have mechanisms similar in many respects to those for the corresponding gaseous reactions [THIS JOURNAL, **56,** 269 (1934)].

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SASKATCHEWAN
SASKATOON, SASK., CANADA
J. W. T. SPINKS
H. TAUBE

RECEIVED APRIL 22, 1937

NEW BOOKS

The Chemistry of Natural Products Related to Phenanthrene. By L. F. FIESER, Associate Professor of Chemistry, Harvard University. Second edition, with an appendix. Reinhold Publishing Corporation, 330 West 42d Street, New York, N. Y., 1937. xiv + 456 pp. 15.5 × 23.5 cm. Price, $7.00.

The increased activity and interest in the field of phenanthrene and related compounds have led the authors of this useful and widely accepted book to supplement the second edition with an appendix. This consists of about 90 pages devoted to a description and discussion of the published investigations during 1936.

The topics are grouped in individual chapters which correspond to those in the main portion of the book. They are too numerous to review here but they include the important contributions to the structure of Vitamin D and the stereochemical nomenclature of the sterols, androsterone and analogous compounds. This additional part has been written with the same clarity and completeness as characterized the original work.

The second edition of this book will be of inestimable value to the investigator or scholar in this general field, as it offers a comprehensive résumé of the literature up to January 1, 1937.

ROGER ADAMS

Reagent Chemicals and Standards, with Methods of Assaying and Testing them; also the Preparation and Standardization of Volumetric Solutions and Extensive Tables of Equivalents. By JOSEPH ROSIN, Chief Chemist and Chemical Director, Merck & Company, Inc. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y., 1937. x + 530 pp. 16 × 23.5 cm. Price, $6.00.

This volume is a thoroughly modern and carefully edited treatment of approved methods for testing the commoner chemical reagents, and the standards of purity to be sought. The author, working from the Merck-Krauch book originally published in 1888, the Murray treatise of 1919, reprinted in 1927, and the reports of the American Chemical Society Committee on analytical reagents, has organized into a single accessible source the most recent information regarding reliable methods and tests.

The greater part of the volume is composed of monographs on reagents and their tests, arranged alphabetically. The substances treated include many new organic reagents. Preceding this section several pages are devoted to describing test solutions, and following it are some fifty pages of stoichiometric data including sections on the determination of the hydrogen-ion concentration, on buffer solutions, indicators and related data. A particularly valuable feature is the inclusion of assay tests for many of the reagents discussed.

In his preface the author calls attention to two interesting facts. First, the purity of commercial reagent chemicals has been greatly increased since the earlier books were issued. Second, the methods of testing quantitatively for impurities have been so improved that often tenths or hundredths of a milligram may now be determined instead of milligrams as was formerly the case.

The author is well equipped to issue such a book, for it was due chiefly to his careful and persistent work that the reagent chemicals issued by the Powers–Weightman–Rosengarten Company during the last years of that firm's independent existence, came in general to be recognized as the purest commercially available.

This book will of necessity become a part of the library of every testing, research and educational laboratory.

WILLIS A. BOUGHTON

An Introduction to Nuclear Physics. By N. FEATHER, Ph.D., University Lecturer in Physics and Fellow of Trinity College, Cambridge. Cambridge University Press; The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1936. x + 212 pp. 21 figs. 14.5 × 22.5 cm. Price, $3.00.

As a result of a vast activity in physical research laboratories in the past decade a definite science of "nuclear physics" has come into being. It has all happened so rapidly that it is now impossible to get a grasp of these developments directly from the journal literature. Dr. Feather has provided an admirable summary of the subject which will be read with profit and pleasure by many whose principal interests lie in other directions as well as by those who are actively engaged in nuclear research.

An outstanding quality of the book is its careful emphasis on the logical sequence of the ideas leading up to current theoretical views. The way in which this has been accomplished in a wholly non-mathematical way is truly marvellous. In general this is the outstanding feature of the presentation which makes it so valuable an introduction, for the account is not burdened with technical details of experiments or of mathematical calculations.

The book is divided into four parts: I. *Introductory* reviews the experimental methods of the older studies of radioactivity and the newer methods with artificially accelerated particles, the growth of the understanding of the nuclear atom model as affected by wave mechanics and the picture of the nucleus as a structure composed of elementary particles; II. *Concerning Stable Nuclei* deals with measurements of mass charge, spin, and magnetic moment of the nuclei of naturally occurring atoms; III. *Concerning Unstable Nuclei* deals with the emission of alpha particles, positive and negative electrons, and gamma rays from radioactive nuclei; IV. *Transformations Produced by Fast-moving Particles and by Radiation* deals with effects produced by bombardment of alpha particles from natural radioactive materials, by neutron bombardment, by artificially accelerated protons and deuterons and photodisintegrations produced by radiation.

As the scope of a book is also indicated by mentioning omissions, it may be remarked that there is no discussion of the physics of cosmic rays and very little on the physics of positrons except as they are emitted from positron-active bodies. These omissions are natural enough as not belonging strictly to nuclear physics. A more serious omission is that of the question of relative abundance of the naturally occurring nuclei as studied by the mass spectrograph and by chemical analyses of the earth's crust.

E. U. CONDON

Diffusion. VI. Dans les Liquides. VII. Dans les Gels et les Solides. (Diffusion in Liquids, Gels and Solids.) (Traité de chimie physique appliqué à la biologie, Ch. VI et VII de Tome I.) By J. DUCLAUX, Professeur au Collège de France. Hermann et Cie., 6 Rue de la Sorbonne, Paris, France, 1936. VI: 90 pp. 35 figs. 16.5 × 25 cm. Price, 20 fr. VII: 50 pp. 8 figs. 16.5 × 25 cm. Price, 12 fr.

The physical chemist interested in diffusion will find these two books useful primarily on account of the extensive bibliographies included. They could also be used to advantage to supplement an advanced course in physical chemistry for either chemists, pre-medical students or biologists. The books contain a rather sketchy presentation of the theoretical side of diffusion, a discussion of experimental methods and a fairly detailed presentation of results for various typical cases. Of particular interest to the biochemist is of course the section on diffusion in gels on account of the obvious importance of membrane equilibria in biological processes.

R. M. FUOSS

Thermodynamic Properties of Steam, Including Data for the Liquid and Solid Phases. By JOSEPH K. KEENAN, Associate Professor of Mechanical Engineering, and FREDERICK G. KEYES, Director of Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology. John Wiley and Sons, 440 Fourth Ave., New York, N. Y., 1936. 89 pp. Illustrated. 19 × 26 cm. Price, $2.75.

This book contains the most extensive and the most accurate available tabulation of the thermodynamic properties of steam.

The specific volume, heat content and entropy along the saturation curve are given for liquid and vapor to the critical point, 705.40°F. and 3206.2 lb./sq. in. As is customary, these quantities are tabulated for integral values of both temperature and pressure.

TABLE I

CORRECTIONS FOR THE ROTATIONAL DISTORTION OF THE WATER MOLECULE

Saturation

Temp., °F.	Enthalpy			Entropy			
t	Sat. liq. h_f	Evap. h_{fg}	Sat. vap. h_g	Sat. liq. S_f	Evap. S_{fg}	Sat. vap. S_g	$\frac{h_{fg}}{T}$
32	0.00	1075.8	1075.8	0.0000	2.1877	2.1877	2.1880
32 corr.	(0.00)	1075.5	1075.5	(0.0000)	2.1873	2.1873	2.1874
212	180.07	970.3	1150.4	0.3120	1.4446	1.7566	....
212 corr.	(180.07)	(970.3)	(1150.4)	(0.3120)	(1.4446)	(1.7566)	....
500	487.8	713.9	1201.7	0.6887	0.7438	1.4325	....
500 corr.	488.4	(713.9)	1202.3	.6894	(0.7438)	1.4332	....
705.4	902.7	0	902.7	1.0580	0	1.0580	....
705.4 corr.	903.8	(0)	903.8	1.0592	(0)	1.0592	....

Superheated Vapor

Abs. press., lb./sq. in.		Temperature, degrees Fahrenheit			
		400	800	1200	1600
14.696	h	1239.9	1432.3	1637.5	1857.3
	h corr.	1240.3	1433.7	1640.4	1862.0
	S	1.8743	2.0576	2.1989	2.3174
	S corr.	1.8748	2.0591	2.2014	2.3209
5500	h	....	985.0	1518.2	1788.1
	h corr.	....	986.4	1521.1	1792.8
	S	....	1.1093	1.4908	1.6369
	S corr.	....	1.1108	1.4933	1.6404

For superheated steam the tabulation extends to 1600°F. and 5500 lb./sq. in.

The properties of the gas have been obtained principally by an analytical treatment based on an equation of state. It is necessary to have a very accurate equation of state in order to make a reliable calculation of the changes in entropy and heat content with pressure, since the procedure requires that first derivatives be accurate. However, one of the most exacting tests of an equation of state is its use in evaluating such a quantity as the change in heat capacity with pressure since this requires reliable second derivatives. The authors apply this test and find excellent agreement with the available experimental data, which extend to a pressure of 3000 lb./sq. in. and a temperature of 900°F. This significant comparison is appropriately presented as Fig. 1 of the book and it says much for the reliability of the heat content (enthalpy), entropy and volume relationships.

The heat capacity of the gas at zero pressure was taken from the computations of A. R. Gordon. These are based on band spectrum data and are more reliable than values which have been obtained in any other way. Nevertheless, there exists a small inaccuracy in the spectroscopic computations of Gordon [*J. Chem. Phys.*, **2**, 65 (1934)]. While the amount of the inaccuracy is too small to be of importance in engineering calculations, it proves to be of some interest.

Gordon based his calculations of various thermodynamic quantities of steam on the assumption that the water molecule could be treated as a rigid rotator; however, he recognized that molecular vibration and rotation are not independent, by using equations which expressed the moments of inertia as a function of the amount and type of vibration. He did not consider the deformation produced by the rotation of the water molecule. This not only changes the kinetic energy due to the alteration of the moments of inertia but also introduces potential energy changes.

The effect of rotational distortion has been considered by E. B. Wilson, Jr., [*ibid.*, **4**, 526 (1936)] and on page 16, Keenan and Keyes mention a personal communication from Wilson. Presumably because they were not available in time, the simple corrections of Wilson were not included in the tables. In any case, it seems worth while to consider their consequences.

The authors selected the data at the normal boiling point of water in order to evaluate the relationship between the liquid and gas states. Applying Wilson's equations it may be shown that a correction of $2.50 \times 10^{-6} (t_F - 212)$ B. t. u. per deg. Fahr. per lb. should be added to the entropy and the quantity $1.25 \times 10^{-6} (T_F^2 - 671.69^2)$ B. t. u. per lb., where $T_F = 459.69 + t_F$, should be added to the heat content of the gas. As will be seen below the above corrections remove a small discrepancy noted by the authors who state on page 19, "The result . . . (heat of vaporization/T) . . . differs by 3 in the last figure given in the tables or about one part in 7000 of the entropy of the vapor at 32°F. Though this difference is negligible for all uses of the tables it signifies certain defects in our knowledge of water vapor at low temperatures."

The application of Wilson's equations in the region near the critical point shows that the heat content and entropy are changed only by about 0.1%. In Table I a few comparisons are given to show the order of magnitude of the above corrections. In order to preserve the self-consistency of the tables, the above corrections for entropy and heat content have been added to the values for the saturated liquid between 212°F. and the critical temperature. This is certainly within the limit of accuracy with which the properties of the liquid are known at these temperatures. For example, the values of entropy and heat content at the critical point given in the present tables are about 2% lower than those given by Keenan in his 1930 tables. It will be evident from the comparisons in Table I that application of the rotational deformation correction of the water molecule is unnecessary for engineering purposes.

By comparing the 32° values of S_{fg} with h_{fg}/T_F in Table I, it is seen that the corrected values are in agreement within the limits of calculation error whereas the uncorrected values show the 0.0003 discrepancy which the authors have pointed out.

The book contains a table giving the properties of liquid water under pressures to 6000 lb./sq. in. and extending to the critical temperature. The properties of ice and water vapor, along the saturation curve, are given to −40°F. Tables of viscosity, heat conductivity, 8 graphs, a Mollier chart, approximately 2 by 3 ft., and a small temperature entropy chart are included.

W. F. GIAUQUE

Solutions of Electrolytes, with Particular Application to Qualitative Analysis. Second edition. By LOUIS P. HAMMETT, Ph.D., Professor of Chemistry in Columbia University. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, N. Y., 1936. ix + 238 pp. Illustrated. 14.5 × 21 cm. Price, $2.25.

In this second edition of Professor Hammett's text-book the material of the first edition has been rearranged and increased. The book is divided into two parts, the first being a modern and thorough treatment of the theory of solutions of electrolytes, and the second part a sketchy laboratory manual for qualitative analysis. Exercises and suggestions for reading are given at the ends of the chapters and lecture experiments are described in an appendix.

The most important change in the new edition comes in the introduction. The Brönsted concept of acids and bases is introduced and employed consistently through the book. The ionization of an acid is treated as the transfer of a proton from the acid to a solvent molecule rather than as a simple dissociation. The writer cannot agree with the author's statement that the newer theory is at least as simple and teachable as the older one; certainly not for students who have had the misfortune to learn the older theory in elementary chemistry. However, there can be no doubt of the value of the newer theory. Professor Hammett is to be congratulated as heartily upon its introduction as upon his modern and simple treatment of the complete ionization of salts, which is common to both editions.

In Chapter II the solubility product principle is discussed, and in Chapter III the law of chemical equilibrium for weak electrolytes. After as thorough a theoretical treatment of both subjects as is possible without the aid of thermodynamics, application of the principles to analytical chemistry is discussed. In Chapter IV, on the ionization of water, the subject of hydrolysis is taken up. It may be noted in passing that the treatment of the hydrolysis of acid salts is not correct. In sodium bicarbonate, the example chosen to illustrate the topic, the amount of ionization of the bicarbonate ion is approximately equal to the amount of hydrolysis. As a result the true concentration of hydroxyl is only one twenty-fifth of that found on page 90. The ionization constants employed here and some of the others given in Table IV on page 60 have not been brought up to date with the new edition.

These are the only flaws which have been noted in this excellent work. Chapter V, on complex compounds, and Chapter VI, on oxidation–reduction reactions, are rich mines of chemical information into which candidates for the doctorate have been seen to delve. Chapter VII, at the end of the theoretical part, deals with oxidation potentials. It is so clearly put and valuable that the writer usually skips to it immediately after Chapter I in a course employing this text.

This is not an easy text. It demands careful study and close attention from the student. It is far superior in its scope and modern viewpoint, however, to any other text in the field.

CHARLES H. GREENE

Structure and Molecular Forces in Pure Liquids and Solutions. A General Discussion. Reprinted from the "Transactions of the Faraday Society." Published for the Faraday Society by Gurney and Jackson, 33 Paternoster Row, London, England, 1937. ii + 282 pp. Illustrated. 16 × 25 cm. Price, 12s./6d., postage 8d.

This volume is a collection of papers presented at the Sixty-fifth General Discussion of the Faraday Society, held in Edinburgh in September, 1936. The papers provide a very comprehensive survey of present knowledge concerning the structure of pure liquids and of non-electrolyte solutions.

The first part of the Discussion, introduced by James Kendall, is devoted to the properties of pure liquids. The heat capacity and viscosity of liquids, their infrared and Raman spectra, and the propagation of ultrasonic waves through them receive considerable attention. The problem of fusion is considered by several authors. There is a noteworthy theoretical discussion of molecular distribution in liquids by J. D. Bernal.

The second part of the Discussion, introduced by J. H. Hildebrand, is concerned with the properties of liquid solutions. The influence of various types of intermolecular force on deviations from ideal behavior in non-electrolyte solutions is the chief topic of discussion.

Those interested in the theory of solutions and in the nature of the liquid state will find the book a valuable source of information.

J. G. KIRKWOOD

Magnetochemie. (Magnetochemistry.) By Dr. WILHELM KLEMM, Professor in the Technical Institute of Danzig-Langfuhr. Akademische Verlagsgesellschaft m. b. H., Leipzig C 1, Germany, 1936. xv + 262 pp. 99 figs. 16 × 23.5 cm. RM. 16; bound, RM. 18.

As a result of the development of the theory of the relation between the magnetic properties and electronic structure of substances, there has occurred during the last decade great progress in the application of magnetic methods to the solution of chemical problems. Klemm's small book on magnetochemistry contains the most extensive and detailed discussion of this field which exists, one hundred pages being devoted to general magnetochemistry, including topics such as Pascal's rules, free radicals and biradicals, the determination of valence states in anomalous compounds [$(NH_4)_2SbBr_6$, perchromates, KO_2, etc.], bond types in coördination complexes, the diamagnetic anisotropy of aromatic crystals, chemical analysis by magnetic methods, etc. A compilation of existent magnetic data is not given; as the author mentions, a complete compilation of these data is badly needed.

This part of Klemm's book is preceded by a well-written elementary discussion of experimental methods, the theory of magnetism and atomic structure, and the diamagnetism, paramagnetism, and ferromagnetism of substances.

Because of its emphasis on chemical applications of magnetic methods, the book provides a useful supplement to the larger treatises of Stoner and Van Vleck.

LINUS PAULING

Enzyme Chemistry. By HENRY TAUBER, Ph.D., Consulting Chemist. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1937. xii + 243 pp. 28 figs. 15.5 × 23.5 cm. Price, $3.00.

Dr. Tauber has rewritten and expanded into book form the material of his earlier "Experimental Enzyme Chemistry."[1] The current edition retains all the merits of the former edition and includes, in addition, an excellent discussion of such recent work as the relationship between the yellow enzyme and lactoflavin, and the enzyme "destroying" vitamin A and ascorbic acid. The author has presented an excellent summary of recent advances in enzyme chemistry and the book is highly recommended.

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[1] Reviewed in THIS JOURNAL, **58**, 2657 (1936).

W. M. SANDSTROM

BOOKS RECEIVED

April 15, 1937–May 15, 1937

HAMILTON FISH ARMSTRONG. "'We or They.' Two Worlds in Conflict." The Macmillan Company, 60 Fifth Ave., New York, N. Y. 106 pp.

WALTER H. EDDY AND GILBERT DALLDORF. "The Avitaminoses. The Chemical, Clinical and Pathological Aspects of the Vitamin Deficiency Diseases." The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Md. 338 pp. $4.50.

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